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Nomenclature of Amino-acids

The following rules have been agreed upon between the Editors of the *Journal of the Chemical Society* and of the *Biochemical Journal*, after consultation with their American colleagues. The examples are given solely to illustrate the application of the rules; in other respects (e.g. the method of enumeration of carbon atoms) names will naturally follow the customary usages of the journal in which they are to appear.

RULE 1. In cases where no possibility of misunderstanding can arise regarding which isomer of the amino-acid is under discussion, the amino-acid may be named without prefix or symbol to denote the direction of the rotation.

RULE 2. In cases where distinction between the stereoisomers is necessary, or considered desirable for the sake of clarity, the configurational family to which the *alpha carbon atom* belongs should be designated by a prefixed *small capital letter*. An additional sign to denote the direction of the rotation is not necessary.

Examples: L-leucine, D-valine.

The optically inactive mixture or racemic compound should, except where Rule 1 applies, be designated with the prefix DL.

Example: DL-leucine.

RULE 3. The configuration of carbohydrates and other compounds which can be configurationally related to glyceraldehyde is designated by a prefixed D or L. Where confusion is possible between the use of the small capital letter prefix for the configuration of the *alpha carbon atom* in amino-acid nomenclature and for that of the highest numbered asymmetric carbon atom in carbohydrate nomenclature, a subscript is added to the small capital letter prefix. Where the prefix is used in the amino-acid sense, the subscript '*s*' is added; where the prefix is used in the carbohydrate sense, the subscript '*g*' is added. These subscripts refer, respectively, to serine, the fundamental substance to which amino-acids that bear structural resemblance to the carbohydrates can be formally related, and to glyceraldehyde, the fundamental substance to which the configuration of the carbohydrates is formally related.

Examples: L_s-threonine, for which the synonym in carbohydrate nomenclature is 2-amino-2:4-dideoxy-D_g-threonic acid; D_s-threonine, for which the synonym is 2-amino-2:4-dideoxy-L_g-threonic acid; L_s-*allo*threonine, for which the synonym is 2-amino-2:4-dideoxy-L_g-erythronic acid; D_s-*allo*threonine, for which the synonym is 2-amino-2:4-dideoxy-D_g-erythronic acid.

Papers that deal with both carbohydrates and amino-acids and which make use of the prefixes should employ subscripts at least for the names of the amino-acids. The acids derived from amino sugars should be named in conformity with carbohydrate nomenclature but with the use of the subscript: e.g. D_g-glucosaminic acid for 2-amino-2-deoxy-D_g-gluconic acid.

RULE 4. If the configurational relationship of the *alpha carbon atom* has not been definitely established, the actual direction of the rotation in a specified solvent, preferably of the free amino-acid in water, is designated by the prefixes *dextro* or *laevo* or, alternatively, by a plus or a minus sign enclosed in parenthesis.

Examples: *dextro*hydroxytryptophan, (+)-hydroxytryptophan.

RULE 5. The prefix *meso* should be used for the *meso* isomers of amino-acids and their derivatives that are optically inactive because of internal compensation.

Example: *meso*lanthionine, *meso*cystine.

RULE 6. Where the amino-acid has two asymmetric centres, but where internal compensation is impossible, the form which occurs in proteins should be called the L-amino-acid, and the form which has opposite configuration on both asymmetric carbon atoms should be designated the D-amino-acid. The pair having opposite configurations on one asymmetric centre only should be designated D-*allo* and L-*allo*, D and L referring as usual to the *alpha carbon atom*.

Examples: D-*allo*threonine, L-*allo*hydroxyproline.

RULE 7. Derivatives and salts of amino-acids and peptides should, where necessary, be named with the use of D or L to denote the configurational family of the *alpha carbon atom* or *atoms*, the customary rules being otherwise observed.

Examples: acetyl-L-tryptophan, L-histidine monohydrochloride monohydrate, copper L-aspartate, D-leucyl-D-valine.

RULE 8. Where a trivial name is applied to a compound that contains two alpha amino carboxylic acid groupings attached to dissimilar carbon chains, the configurational designation is that of the *alpha carbon atom* of the *smaller of the two chains*.

Examples: D-cystathionine for *S*-(D-β-amino-β-carboxyethyl)-D-homocysteine, L-*allo*cystathionine for *S*-(L-β-amino-β-carboxyethyl)-D-homocysteine.

It is emphasized that the introduction of new trivial names should be avoided.

CONTENTS.

PAPERS COMMUNICATED TO THE CHEMICAL SOCIETY.

General, Physical, and Inorganic.

PAGE

187. The Crystal Structure of the Orthorhombic Modification of 1 : 2 : 5 : 6-Dibenzanthracene. A Quantitative *X*-Ray Investigation.
By J. Monteath Robertson and J. G. White 1001

188. The Chemistry of Plutonium.
By B. G. Harvey, H. G. Heal, A. G. Maddock, and (Miss) E. L. Rowley . 1010

203. The Preparation; Properties, and Chlorination Products of Carbon Diselenide.
By D. J. G. Ives, R. W. Pittman, and W. Wardlaw 1080

204. The Relation of Yttrium to the Lanthanons: A Study of Molecular Volumes.
By Joseph K. Marsh 1084

Organic.

186. Photochemical Reactions in Sunlight. Part XII. Reactions with Phenanthraquinone, 9-Arylxanthens, and Diphenyl Triketone.
By Alexander Schönberg and Ahmed Mustafa 997

189. Production of Antibiotics by Fungi. Part III. Javanicin. An Antibacterial Pigment from *Fusarium javanicum*.
By H. R. V. Arnstein and A. H. Cook 1021

190. The Course of Cyclisation in the Formation of Alicyclic Rings. Part I. Effect of Alkyl Groups on the Cyclisation of Esters of Polycarboxylic Acids.
By R. N. Chakravarti 1028

191. Olefinic Acids. Part II. The Reactivity of α-Bromoacrylic Acid and Some Related Compounds.
By L. N. Owen and H. M. Babatunde Somade 1030

192. Tetrahydroacridones and Related Compounds as Antimalarials.
By (Miss) J. M. L. Stephen, (Miss) I. M. Tonkin, and James Walker . . 1034

193. β-Phellandrene Tetrabromide.
By P. A. Berry and A. Killen Macbeth 1039

194. Molecular Rearrangement and Displacement of Arylamine Residues in α-Arylamino-ketones. Part I.
By R. M. Cowper and T. S. Stevens 1041

195. Experiments with Diazomethane and its Derivatives. Part XIII. Action of Diazomethane on Hydroxyanils.
By Alexander Schönberg, Ahmed Mustafa, and (in part) Mustafa Kamal Hilmy 1045

196. The Quantitative Determination of Galactose, Mannose, Arabinose, and Rhamnose.
By E. L. Hirst, J. K. N. Jones, and E. A. Woods 1048

197. A Synthesis of Cytidine.
By G. A. Howard, B. Lythgoe, and A. R. Todd 1052

198. The Constitution of Cherry Gum. Part II. The Products of Hydrolysis of Methylated Cherry Gum.
By J. K. N. Jones 1055

199. Some Reactions and Derivatives of 6- and 7-Nitro-2-naphthylamines. Part II. Nitration and Diazo-coupling.
By Herbert H. Hodgson and Edward R. Ward 1060

200. The Synthesis of 3-Methyl and 3 : 5-Dimethyl *l*-Arabinose.
By E. L. Hirst, J. K. N. Jones, and (Miss) E. Williams 1062

201. The Constitution of Egg-plum Gum. Part I.
By E. L. Hirst and J. K. N. Jones 1064

202. The Hydrogenation of Furfuraldehyde to Furfuryl Alcohol and Sylvan (2-Methylfuran).
By John G. M. Bremner and Richard K. F. Keeys 1068

PAGE

205. The Preparation and Ultra-violet Light Absorption of Some Substituted Phenylpropenyl- and Styrylmethyl-carbinols and 1-Phenylbutadienes.
By ERNEST A. BRAUDE, E. R. H. JONES, and E. S. STERN 1087

206. The Kinetics of Anionotropic Rearrangement. Part VI. The Effects of Methyl, Methoxy-, and Halogen Substituents attached to a Phenyl Group.
By ERNEST A. BRAUDE and E. S. STERN 1096

207. Studies in Light Absorption. Part IV. Nitro-olefins.
By ERNEST A. BRAUDE, E. R. H. JONES, and G. G. ROSE 1104

208. Syntheses in the Thiopyran Series. Part I. Tetrahydro-derivatives.
By RALPH F. NAYLOR 1106

NOTES—Activating Influence of *para*-Groups on the Lability of Chlorine in Chlorobenzenes.
By G. M. BADGER, J. W. COOK, and (MISS) WENDY P. VIDAL 1109

An Improved Preparation of 1 : 8-Dinitronaphthalene.
By HERBERT H. HODGSON and EDWARD R. WARD 1109

OBITUARY NOTICE 1110

INDEX OF AUTHORS' NAMES.

ARNSTEIN, H. R. V., and Cook, A. H., 1021.
Badger, G. M., Cook, J. W., and Vidal, (Miss) W. P., 1109.
Berry, P. A., and Macbeth, A. K., 1039.
Braude, E. A., Jones, E. R. H., and Rose, G. G., 1104.
Braude, E. A., Jones, E. R. H., and Stern, E. S., 1087.
Braude, E. A., and Stern, E. S., 1096.
Bremner, J. G. M., and Keeys, R. K. F., 1068.
Chakravarti, R. N., 1028.
Cook, A. H. See Arnstein, H. R. V.
Cook, J. W. See Badger, G. M.
Cowper, R. M., and Stevens, T. S., 1041.
Harvey, B. G., Heal, H. G., Maddock, A. G., and Rowley, (Miss) E. L., 1010.
Heal, H. G. See Harvey, B. G.
Hilmy, M. K. See Schönberg, A.
Hirst, E. L., and Jones, J. K. N., 1064.
Hirst, E. L., Jones, J. K. N., and Williams, (Miss) E., 1062.
Hirst, E. L., Jones, J. K. N., and Woods, E. A., 1048.
Hodgson, H. H., and Ward, E. R., 1060, 1109.
Howard, G. A., Lythgoe, B., and Todd, A. R., 1052.
Ives, D. J. G., Pittman, R. W., and Wardlaw, W., 1080.
Jones, E. R. H. See Braude, E. A.
Jones, J. K. N., 1055.
Jones, J. K. N. See also Hirst, E. L.
Keeys, R. K. F. See Bremner, J. G. M.
Lythgoe, B. See Howard, G. A.
Macbeth, A. K. See Berry, P. A.
Maddock, A. G. See Harvey, B. G.
Marsh, J. K., 1084.
Mustafa, A. See Schönberg, A.
Naylor, R. F., 1106.
Owen, L. N., and Somade, H. M. B., 1030.
Pittman, R. W. See Ives, D. J. G.
Robertson, J. M., and White, J. G., 1001.
Rose, G. G. See Braude, E. A.
Rowley, (Miss) E. L. See Harvey, B. G.
Schönberg, A., and Mustafa, A., 997.
Schönberg, A., Mustafa, A., and Hilmy, M. K., 1045.
Somade, H. M. B. See Owen, L. N.
Stephen, (Miss) J. M. L., Tonkin, (Miss) I. M., and Walker, J., 1034.
Stern, E. S. See Braude, E. A.
Stevens, T. S. See Cowper, R. M.
Todd, A. R. See Howard, G. A.
Tonkin, (Miss) I. M. See Stephen, (Miss) J. M. L.
Vidal, W. P. See Badger, G. M.
Walker, J. See Stephen, (Miss) J. M. L.
Ward, E. R. See Hodgson, H. H.
Wardlaw, W. See Ives, D. J. G.
White, J. G. See Robertson, J. M.
Williams, (Miss) E. See Hirst, E. L.
Woods, E. A. See Hirst, E. L.

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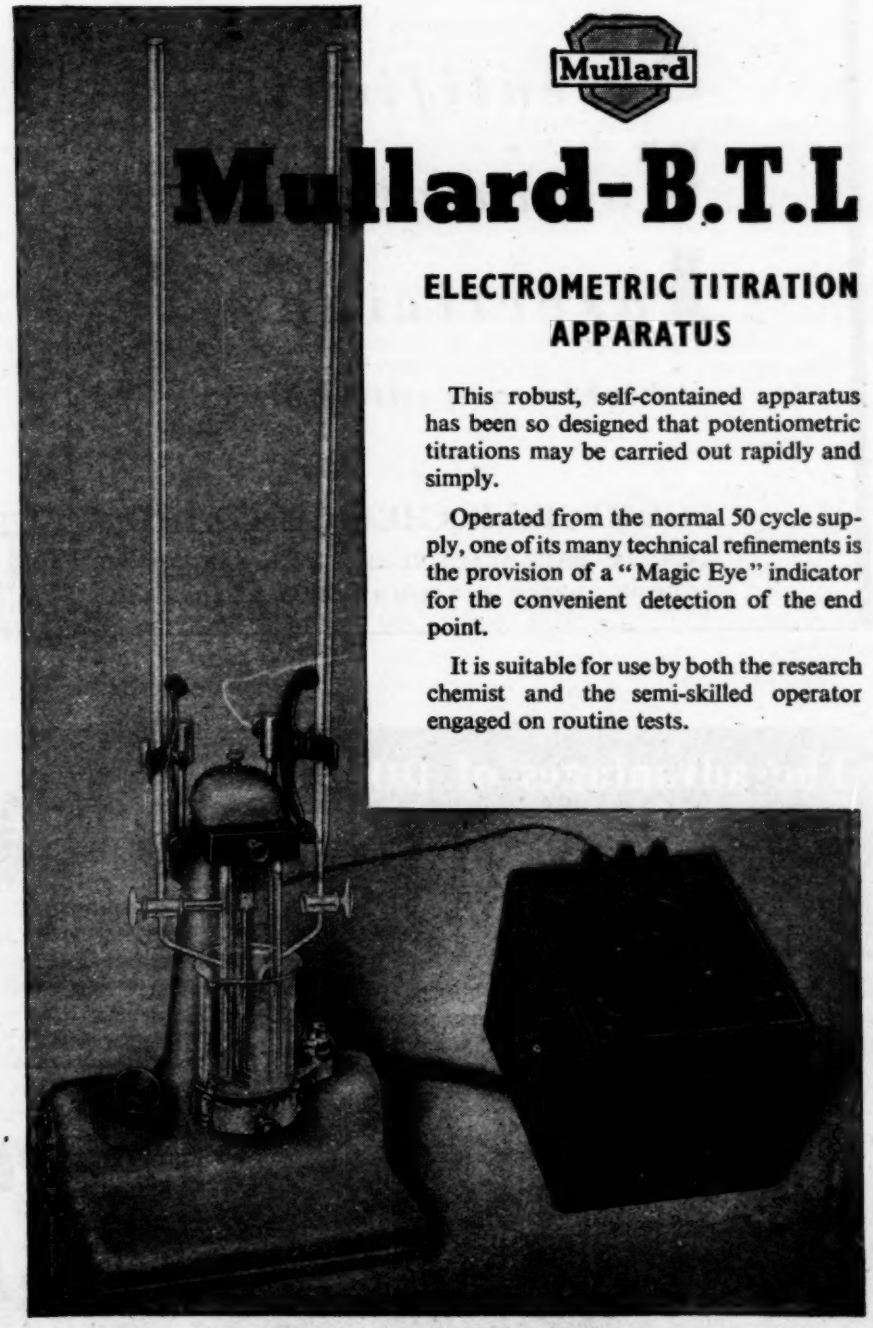

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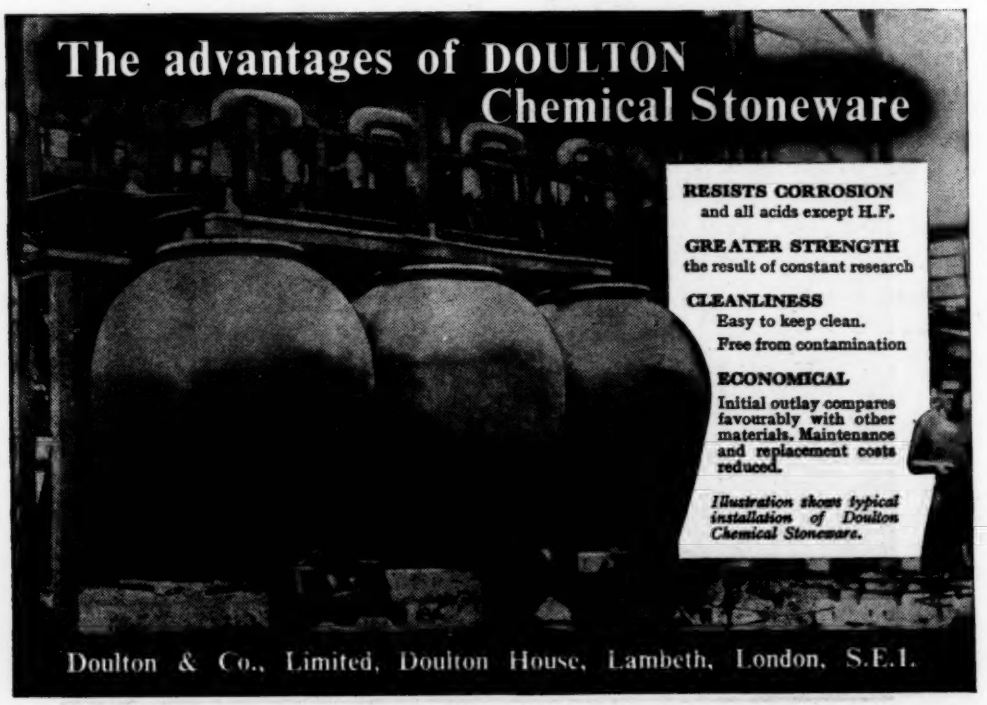
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186. *Photochemical Reactions in Sunlight. Part XII. Reactions with Phenanthraquinone, 9-Arylxanthens, and Diphenyl Triketone.*

By Alexander Schönberg and Ahmed Mustafa.

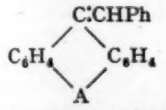
(*a*) The photochemical addition of phenanthraquinone or retenequinone to various substances containing an olefinic linkage has been carried out. The olefinic compounds include diphenylketen and a number of olefins, (I)—(III), in which one carbon atom of the ethylenic linkage is a member of a five- or six-membered ring system. The photo-products obtained are represented by the formulæ (V)—(VIII).

(*b*) Reaction scheme (A), which shows the photo-formation of peroxides from 9-arylxanthens, was carried out in five cases. Some of the arylxanthens are new and were prepared according to scheme (B). 9-Benzylxanthen was stable in sunlight in the presence of oxygen.

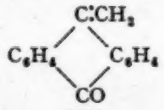
(*c*) The photo-reaction between phenanthraquinone and aromatic aldehydes was studied in three cases (see C); steric hindrance (ortho-effect) may explain the slow rate of the photo-reaction in the case of 2-methoxy-1-naphthaldehyde.

(*d*) Diphenyl triketone in sunlight forms benzil.

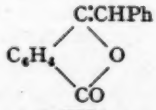
(*a*) Recently (*J.*, 1944, 387; 1945, 551) we showed that phenanthraquinone reacted with certain unsaturated compounds to form derivatives of phenanthro-1 : 4-dioxen. We have now extended this reaction to 9-benzylidene-xanthen and -thioxanthen (I, *a* and *b*), methyleneanthrone (II), benzylidenephthalide (III), 1 : 1-di-*p*-anisylpropylene (IV*a*), 1 : 1-dixenylpropylene (IV*b*), *as.*-dixenylethylene (IV*c*), and diphenylketen.



(I*a*, A=O; I*b*, A=S.)



(II.)



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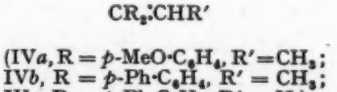
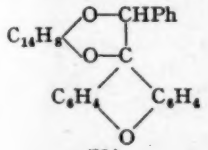


(IV*a*, R = *p*-MeO·C$_6$H$_4$, R′=CH$_3$; IV*b*, R = *p*-Ph·C$_6$H$_4$, R′ = CH$_3$; IV*c*, R = *p*-Ph·C$_6$H$_4$, R′ = H.)

The photo-*product* obtained from (I*a*) has the structure (V), and those from (I*b*), (II), and (III) are analogous. Those from (IV, *a*, *b*, and *c*) are of type (VI), in which R and R′ are as in the three formulæ. Diphenylketen gives the *compound* (VII). The condensation *product* from



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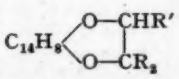

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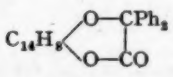

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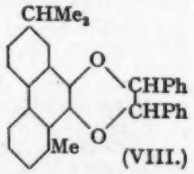
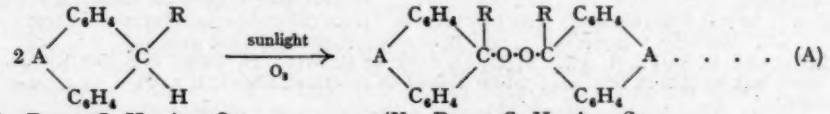


(VIII.)

retenequinone and stilbene is assigned the structure (VIII). All these products are colourless except (VIII), which is light yellow. On pyrolysis, the compounds were resolved into their generators except that diphenylketen was not obtained from (VII), probably because of its thermolability.

The photo-products from (III) and diphenylketen were insoluble in aqueous sodium hydroxide, but were readily attacked when heated with aqueous-alcoholic sodium hydroxide, a behaviour according with the lactone structure assigned to them; the resulting solutions were orange-coloured.

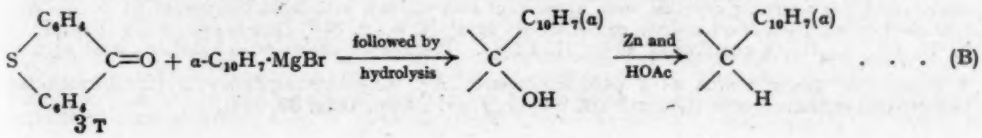
(*b*) To the list of triarylmethanes forming peroxides in air and sunlight by route (A) (Schönberg and Mustafa, *J.*, 1945, 657), we now add 9-α-*naphthylthioxanthen*, 9-m-*tolylxanthen*, and 9-*p*-tolyl-, 9-*p*-anisyl-, and 9-α-naphthyl-xanthen. The first two are new and were prepared as shown in (B) for the naphthyl compound :



(IX*a*, R = α-C$_{10}$H$_7$, A = S; IX*b*, R = *m*-C$_6$H$_4$Me, A = O.)

(X*a*, R = α-C$_{10}$H$_7$, A = S; X*b*, R = *m*-C$_6$H$_4$Me, A = O.

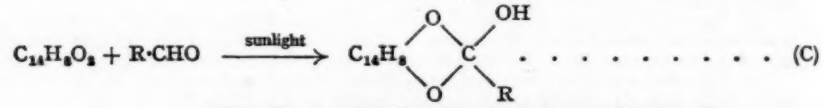
. . . . (A)



. . . (B)

9-Benzylxanthen in benzene was unchanged when exposed to sunlight in presence of oxygen. It seems that an aryl group in position 9 in xanthyl is necessary for the formation of peroxides in sunlight by the action of oxygen.

(*c*) Schönberg and Moubasher (*J.*, 1939, 1430) described a number of photo-reactions between phenanthraquinone and aromatic aldehydes according to (C). We have carried out similar reactions with 2 : 4-dimethoxybenzaldehyde, 2-methoxy-1-naphthaldehyde, and cuminaldehyde; the first two reactions are much slower than that between benzaldehyde and phenanthraquinone in sunlight: this may be due to steric hindrance (ortho-effect).



(C)

[XI*a*, R=2:4-(MeO)$_2$C$_6$H$_3$; XI*b*, R = 2-(MeO)C$_{10}$H$_6$; XI*c*, R = *p*-C$_6$H$_4$Pr$^\beta$.]

(*d*) Lately, two methods have been described for conversion of diphenyl triketone into benzil by processes in the dark, namely, by the action (i) of aluminium chloride and (ii) of selenium (precipitated) in the presence of oxygen (Schönberg and Azzam, *J.*, 1939, 1430; Schönberg and Moubasher, in the press). It has now been found that the conversion is also effected when a benzene solution of the triketone is exposed to sunlight, but no reaction takes place in the dark in the absence of catalysts.

Experimental.

All substances were in solution unless otherwise stated. The benzene used was free from toluene * and thiophen and had been dried over sodium. The reaction mixtures were placed in a Schlenk tube (Schlenk and Thal, *Ber.*, 1913, **46**, 2655; comp. Houben, "Die Methoden der Organischen Chemie", 2nd Edition, Vol. 4, p. 960) of Pyrex glass, and the air was then displaced by dry carbon dioxide and the tube sealed by fusion.

The photo-formation of peroxides was carried out as above, but in the presence of dry air.

Control experiments in the dark, but otherwise under identical conditions, showed no reaction.

(a, i) *Photo-reactions with Phenanthraquinone.—9-Benzylidenexanthen.* Phenanthraquinone (1 g.) and 9-benzylidenexanthen (I*a*) (Decker, *Ber.*, 1905, **38**, 2493) (1·3 g.) in benzene (50 c.c.) were exposed to sunlight for 4 months (February—June), the phenanthraquinone gradually dissolving completely. The benzene was evaporated off in a vacuum, and the residual dark solid washed with cold acetone and crystallised from benzene–light petroleum (b. p. 30—50°), forming almost colourless crystals, m. p. 241° (red brown melt) (Found: C, 84·8; H, 4·9. $C_{34}H_{22}O_3$ requires C, 85·3; H, 4·6%). The *product* (V), when treated with sulphuric acid, gave an olive-green colour; it was soluble in hot benzene and ligroin (b. p. 100—150°).

Thermal decomposition. The foregoing product was heated for ½ hour at about 270° (bath temp.) in a stream of dry carbon dioxide (the height of the decomposition tube being about 25 cm.); red-brown fumes were evolved, and an orange liquid collected on the walls of the tube. After 24 hours, this solidified to a mixture of orange and almost colourless crystals; extraction with hot light petroleum (b. p. 50—60°) left a residue of phenanthraquinone (identified, after recrystallisation from alcohol, by m. p., mixed m. p., and colour reaction with sulphuric acid). The extract was concentrated, and the resulting crystals, recrystallised from ethyl alcohol, proved to be 9-benzylidenexanthen (I*a*).

9-Benzylidenethioxanthen. Phenanthraquinone (1 g.) and 9-benzylidenethioxanthen (I*b*) (Decker, *loc. cit.*) (1·4 g.) in 30 c.c. of benzene were exposed to sunlight for 3 months (August—November), the phenanthraquinone dissolving as before and the orange colour of the solution fading to pale yellow. The crystals that separated were filtered off, washed several times with hot absolute ethyl alcohol, and recrystallised from benzene, forming colourless crystals, m. p. 245° (orange melt) (Found: C, 82·6; H, 4·6; S, 5·9. $C_{34}H_{22}O_2S$ requires C, 82·6; H, 4·4; S, 6·5%). The *product* (as V) gave a brown colour with sulphuric acid at room temperature; it was difficultly soluble in cold ethyl alcohol, but soluble in hot benzene; when heated as described above, it yielded its generators, which were separated as above.

Methyleneanthrone. Phenanthraquinone (1 g.) and methyleneanthrone (II) (Clar, *Ber.*, 1936, **69**, 1687) (1 g.) in 25 c.c. of benzene were exposed to sunlight for 40 days (February—April); the phenanthraquinone dissolved, and the resulting crystals were filtered off and washed with cold benzene, followed by hot ethyl alcohol; they recrystallised from chlorobenzene, forming almost colourless crystals, m. p. 165° (decomp.; green melt), and gave a bluish-green colour with sulphuric acid. The *product* (as V) (Found: C, 84·1; H, 4·3. $C_{29}H_{18}O_3$ requires C, 84·1; H, 4·4%) is difficultly soluble in hot ethyl alcohol, but soluble in benzene; when heated as described above, it yielded its generators, separated as before.

Benzylidenephthalide. Phenanthraquinone (1 g.) and benzylidenephthalide (III) (*Org. Synth.*, Coll. Vol. 2, p. 61) (1·1 g.) in benzene (25 c.c.) were exposed to sunlight for 20 days (May); the quinone dissolved, and the resulting crystals were filtered off and washed with light petroleum (b. p. 50—60°). The *product* crystallised from xylene in colourless crystals, m. p. 310° (red-brown melt) (Found: C, 80·3; H, 4·1. $C_{29}H_{16}O_4$ requires C, 80·9; H, 4·2%). It gave no colour with sulphuric acid at room

* Toluene in sunlight acts as a reducing agent; *e.g.*, phenanthraquinone is transformed into 9 : 10-dihydroxyphenanthrene (Benrath and Meyer, *J. pr. Chem.*, 1914, **89**, 258).

temperature, but a violet colour at 100°; it was difficultly soluble in cold ethyl alcohol and benzene, but soluble in hot xylene. Its behaviour with alkalis is described on p. 997.

Thermal decomposition was carried out for ½ hour at about 330° (bath temp.) as described above. The resulting mixture was separated as before.

1 : 1-*Di*-p-*xenylpropylene*.—Phenanthraquinone (1 g.) and the olefin (IV*b*) (Pfeiffer and Schneider, *J. pr. Chem.*, 1931, **129**, 129) were exposed to sunlight for 50 days (March—April). The benzene was evaporated off in a vacuum, and the residual dark oil extracted with hot ligroin (b. p. 100—150°). The extract, on slow evaporation in a vacuum, gave crystals, which recrystallised from ethyl alcohol in colourless crystals, m. p. 143° (orange melt) (Found: C, 88·9; H, 5·8. $C_{41}H_{30}O_2$ requires C, 88·8; H, 5·5%). 2 : 2-*Dixenyl*-3-*methylphenanthro*-9′ : 10′-1 : 4-*dioxen* (as VI) when treated with sulphuric acid gave an olive-green colour after a few minutes at room temperature; it was soluble in benzene and hot ethyl alcohol.

The thermal decomposition was carried out as described above for ½ hour at about 270° (bath temp.); the mixture was separated as before.

Diphenylketen. Phenanthraquinone (1 g.) and diphenylketen (Staudinger, *Ber.*, 1911, **44**, 1622) (2 g.) in 30 c.c. of benzene were exposed to sunlight for 3 months (March—May), the phenanthraquinone dissolving as before and the solution becoming brown. The crystals that separated were filtered off, washed with cold benzene, and recrystallised from hot benzene, forming almost colourless crystals, m. p. 227—230° (decomp.; orange melt) (Found: C, 83·5; H, 4·5. $C_{28}H_{18}O_3$ requires C, 83·6; H, 4·5%). The *compound* (VII) gave no immediate colour with sulphuric acid, but a dirty-green colour developed after some time; it was difficultly soluble in ligroin (b. p. 90—100°) and ethyl alcohol, but soluble in hot benzene; for its behaviour with alkali, see p. 997.

Thermal decomposition (15 mins. at bath temp. *ca.* 300°) afforded drops of an orange oil which solidified after 24 hours and were identified as phenanthraquinone.

as.-*Dixenylethylene*. Phenanthraquinone (1 g.) and the ethylene (IV*c*) (1·6 g.) (Pfeiffer and Schneider, *loc. cit.*) were exposed to sunlight for 3 months (March—June). The separated solid was collected, washed with cold ether and then with hot acetone, and recrystallised from benzene in colourless crystals, m. p. 234° (Found: C, 89·5; H, 5·3. $C_{40}H_{28}O_2$ requires C, 88·9; H, 5·2%). 2 : 2-*Dixenylphenanthro*-9′ : 10′-1 : 4-*dioxen* (as VI), when treated with sulphuric acid, gave a red-brown colour at room temperature; it was soluble in hot benzene and difficultly soluble in ligroin (b. p. 90—100°).

For separation of the products of thermal decomposition (15 minutes at bath temp. *ca.* 290°), hot ligroin (b. p. 90—100°), in which (IV*c*) is soluble, was used.

1 : 1-*Di*-p-*anisylpropylene*. Phenanthraquinone (1 g.) and the olefin (IV*a*) (Pfeiffer and Wizinger, *Annalen*, 1928, **461**, 145) (1·1 g.) were exposed to sunlight for 3 months (March—June). The benzene was evaporated off in a vacuum and the brownish oily residue was extracted several times with ligroin (b. p. 70—80°). The extract, on slow evaporation, gave an almost colourless solid residue which recrystallised from benzene–light petroleum (b. p. 50—60°) in colourless crystals, m. p. 181° (orange-brown melt) (Found: C, 80·2; H, 5·6. $C_{31}H_{26}O_4$ requires C, 80·5; H, 5·6%). 2 : 2-*Di*-p-*anisyl*-3-*methylphenanthro*-9′ : 10′-1 : 4-*dioxen* (as VI) when treated with sulphuric acid at room temperature gave a dark brown colour changing after a few minutes into olive-green; it was soluble in hot benzene, difficultly soluble in cold ethyl alcohol.

The products of thermal decomposition (bath temp. *ca.* 270°) were separated as in the preceding case.

(a, ii) *Photo-reaction between Retenequinone and Stilbene*.—Retenequinone (1 g.) and stilbene (0·7 g.) in 25 c.c. of benzene were exposed to sunlight for 21 days (March), the quinone then having dissolved. The benzene was evaporated off in a vacuum, and the solid residue was washed with cold light petroleum (b. p. 80—100°), and crystallised from ethyl alcohol, forming very light yellow crystals, m. p. 224—226° (decomp.; red melt) (Found: C, 86·8; H, 6·5. $C_{32}H_{28}O_3$ requires C, 86·5; H, 6·3%). 5 : 6-*Diphenyl*-(1′-*methyl*-7′-iso*propylphenanthro*)-9′ : 10′-1 : 4-*dioxen* (VIII) gave no colour with sulphuric acid at room temperature, but a red colour at 100° and was soluble in hot benzene. At *ca.* 270° (bath temp.) it decomposed into retenequinone (identified, after recrystallisation from chloroform and ethyl alcohol, by mixed m. p. and colour reaction with sulphuric acid) and stilbene (recrystallised from ethyl alcohol and identified by m. p. and mixed m. p.). (This experiment was carried out with M. Z. Barakat.)

(b) *Action of Oxygen on Triarylmethanes in Sunlight*.—(1) 9-α-*Naphthylxanthen*. Reduction of 9-α-naphthylxanthhydrol (Gomberg and Schoepfle, *J. Amer. Chem. Soc.*, 1917, **39**, 1668) was carried out as described by Ullmann and Engi (*Ber.*, 1904, **37**, 2371) for the phenyl compound, *i.e.*, by means of zinc dust and acetic acid with platinum chloride as a catalyst. 9-α-Naphthylxanthen recrystallised from benzene–light petroleum (b. p. 30—50°), m. p. 184° (Found: C, 89·5; H, 5·1. Calc. for $C_{23}H_{16}O$: C, 89·6; H, 5·2%). Kovache (*Ann. Chim.*, 1918, **10**, 184) gives m. p. 184°. It was soluble in benzene and gave no colour with sulphuric acid.

9-α-Naphthylxanthen was insolated for 5 days (February). The colourless crystals that separated were recrystallised from xylene; m. p. 228° (decomp.; dark melt) (Found: C, 85·3; H, 4·7. Calc. for $C_{46}H_{32}O_4$: C, 85·4; H, 4·7%). For the peroxide, Gomberg and Schoepfle (*loc. cit.*) gave m. p. 228—230°. The peroxide was practically insoluble in light petroleum (b. p. 30—50°) or in cold benzene, but soluble in hot benzene or xylene, and gave a deep red solution with sulphuric acid.

(2) 9-α-*Naphthylthioxanthen*. To a Grignard solution of α-naphthylmagnesium bromide (magnesium, 1·2 g.; α-bromonaphthalene, 10·4 g.; dry ether, 50 c.c.), dry benzene (30 c.c.) was added, and the mixture treated gradually with powdered thioxanthone (Davis and Smiles, *J.*, 1910, **97**, 1296) (6 g.). The solution became yellow and a yellow precipitate formed; the mixture was refluxed for one hour, set aside overnight, poured into ice-cold dilute hydrochloric acid, extracted with ether, the extract dried, and the ether–benzene mixture evaporated. The residue, washed with cold ethyl alcohol and recrystallised from hot ethyl alcohol, had m. p. 191—192° (Found: C, 81·1; H, 4·3; S, 8·8. $C_{23}H_{16}OS$ requires C, 81·2; H, 4·7; S, 9·4%). 9-α-*Naphthylthioxanthhydrol* was soluble in cold benzene, ether, and hot ethyl alcohol, and gave a red colour with sulphuric acid. It was reduced as in the preceding case, and the colourless 9-α-*naphthylthioxanthen* crystallised from benzene with one molecule of solvent of crystallisation, m. p. 77° (Found: C, 86·7; H, 5·5; S, 7·9. $C_{23}H_{16}S,C_6H_6$ requires C, 86·5;

H, 5·4; S, 7·9%). It was freely soluble in benzene, but difficultly soluble in ethyl alcohol; it gave no colour with sulphuric acid.

This xanthen was insolated for 4 days (February). The colourless crystals that separated, recrystallised from benzene–light petroleum (b. p. 30—50°), had m. p. 176° (efferv.). *9-α-Naphthylthioxanthyl peroxide* (Found: C, 81·1; H, 4·4; S, 8·8. $C_{46}H_{30}O_2S_2$ requires C, 81·4; H, 4·5; S, 9·4%) is slightly soluble in hot benzene and soluble in hot xylene and gives a violet colour with sulphuric acid.

(3) 9-m-*Tolylxanthen*. 9-m-*Tolylxanthhydrol*, prepared substantially as for 9-α-naphthylthioxanthhydrol but from *m*-tolylmagnesium bromide (magnesium, 1·2 g.; *m*-bromotoluene, 9 g.; dry ether, 30 c.c.; dry benzene, 30 c.c.) and xanthone (5 g.), separated from benzene in colourless crystals, m. p. 149° (Found: C, 82·8; H, 5·6. $C_{20}H_{16}O_2$ requires C, 83·3; H, 5·5%). It was soluble in hot benzene and difficultly soluble in light petroleum (b. p. 30—50°) and gave a red colour with sulphuric acid.

Reduction of 9-*m*-tolylxanthhydrol was carried out as for the naphthyl analogue. The colourless 9-m-*tolylxanthen*, crystallised from ethyl alcohol, had m. p. 98° (Found: C, 88·1; H, 5·5. $C_{20}H_{16}O$ requires C, 88·2; H, 5·9%). It was difficultly soluble in cold ethyl alcohol, but soluble in hot ethyl alcohol or hot benzene; it gave no colour with sulphuric acid.

9-*m*-Tolylxanthen was insolated for 38 days (February—March), during which the benzene solution became yellow. The colourless crystals, obtained by evaporation of the benzene, followed by washing with absolute ethyl alcohol, were recrystallised from benzene–ethyl alcohol and had m. p. 205°. The *peroxide* (Found: C, 83·2; H, 5·4. $C_{40}H_{30}O_4$ requires C, 83·6; H, 5·2%) was soluble in cold benzene, but insoluble in hot ethyl alcohol; it gave a yellow colour with sulphuric acid.

(4) 9-p-*Tolylxanthen*. Reduction of 9-*p*-tolylxanthhydrol (Gomberg and Cone, *Annalen*, 1909, **370**, 164) was carried out as above. The colourless 9-*p*-tolylxanthen, crystallised from ethyl alcohol, had m. p. 116° (Found: C, 87·7; H, 5·9. Calc. for $C_{20}H_{16}O$: C, 88·2; H, 5·9%) (Kovache, *loc. cit.*, gives m. p. 116°). It gave no colour with sulphuric acid.

9-*p*-Tolylxanthen was insolated for 2 days (April). Colourless crystals, which began to separate after a few hours, were finally recrystallised from benzene; m. p. 217—218° (decomp.) (Found: C, 83·3; H, 5·6. Calc. for $C_{40}H_{30}O_4$: C, 83·6; H, 5·3%). Gomberg and Cone (*loc. cit.*, p. 166) give m. p. 212° (not sharp) for the peroxide. It dissolved with difficulty in light petroleum (b. p. 30—50°) and gave a brownish-red colour with sulphuric acid.

(5) 9-p-*Methoxyphenylxanthen*. Reduction of 9-*p*-methoxyphenylxanthydrol (Gomberg and West, *J. Amer. Chem. Soc.*, 1912, **34**, 1528) was carried out as for the naphthyl analogue. The colourless xanthen, crystallised from ligroin (b. p. 70—80°), had m. p. 117° (Found: C, 82·9; H, 5·5. Calc. for $C_{20}H_{16}O_2$: C, 83·3; H, 5·5%) (Kovache, *loc. cit.*, gives m. p. 115°). It gave no colour with sulphuric acid.

9-*p*-Methoxyphenylxanthen was insolated for 30 days (February—March). The colourless crystals that separated were recrystallised from xylene, m. p. 205° (decomp.; dark brown melt) (Found: C, 79·1; H, 5·2. Calc. for $C_{40}H_{30}O_6$: C, 79·2; H, 4·9%). Gomberg and West (*loc. cit.*) give m. p. 214° (decomp.) for *p*-methoxyphenylxanthyl peroxide. It was soluble in boiling benzene and toluene, slightly soluble in cold benzene, and insoluble in light petroleum (b. p. 30—50°), and gave a red-brown colour with sulphuric acid.

(6) 9-*Benzylxanthen*. 9-Benzylxanthen (Decker, *loc. cit.*) (2 g.) was insolated for four months (April—August) in the presence of air. On slow evaporation of the benzene solution, it was recovered practically unchanged.

(c) *Photochemical Reaction between Phenanthraquinone and Aromatic Aldehydes*.—(i) 2 : 4-*Dimethoxybenzaldehyde*. Phenanthraquinone (1 g.) and the aldehyde (0·8 g.) in benzene (30 c.c.) were exposed to sunlight for 10 days (August). The colourless crystals that separated were washed with small amounts of cold benzene and crystallised from benzene, from which the 2 : 4-*dimethoxyphenylhydroxymethylene ether* of 9 : 10-dihydroxyphenanthrene (XI*a*) separated in colourless needles, m. p. 223° (red brown melt) (Found: C, 73·4; H, 4·8. $C_{23}H_{18}O_5$ requires C, 73·8; H, 4·8%). It was soluble in hot chloroform and benzene and difficultly soluble in hot ethyl alcohol; it gave a green colour with sulphuric acid.

(ii) *Cuminaldehyde*. Phenanthraquinone (1 g.) and cuminaldehyde (0·7 g.) in benzene (30 c.c.) were exposed to sunlight for 6 days (September). The resulting colourless crystals, recrystallised from ligroin (b. p. 80—90°), had m. p. 168—170° (decomp.; red melt). The benzene solution on concentration, gave a further amount of the *cuminylhydroxymethylene ether* of 9 : 10-dihydroxyphenanthrene (XI*c*) (Found: C, 80·1; H, 5·3. $C_{24}H_{20}O_3$ requires C, 80·9; H, 5·6%). It was difficultly soluble in cold ethyl alcohol, but soluble in hot benzene; it gave an olive-green colour with sulphuric acid.

(iii) 2-*Methoxy*-1-*naphthaldehyde*. Phenanthraquinone (1 g.) and 2-methoxy-1-naphthaldehyde (0·9 g.) in benzene (30 c.c.) were exposed for 10 days (September). The benzene was evaporated in a vacuum, and the residue washed with hot ethyl alcohol and crystallised from ligroin (100—150°), forming colourless crystals, m. p. 190° (orange melt) (Found: C, 79·1; H, 4·6. $C_{28}H_{18}O_4$ requires C, 79·1; H, 4·6%). The 2-*methoxy*-1-*naphthylhydroxymethylene ether* of 9 : 10-dihydroxyphenanthrene (XI*b*) was soluble in benzene and difficultly soluble in hot ethyl alcohol; it gave a green colour with sulphuric acid.

(d) *Action of Sunlight on Diphenyl Triketone*.—Diphenyl triketone (2 g.) (*Org. Synth.*, Coll. Vol. 2, p. 244) in benzene (20 c.c.) was exposed to sunlight for 21 days (May). The benzene solution on evaporation in a vacuum, gave a yellow residue. The latter, on crystallisation from ligroin (b. p. 70—80°) gave yellow crystals, m. p. 95°, proved to be benzil (m. p. and mixed m. p.); yield *ca.* 70%. The dark experiment was negative.

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187. *The Crystal Structure of the Orthorhombic Modification of 1 : 2 : 5 : 6-Dibenzanthracene. A Quantitative X-Ray Investigation.*

By J. Monteath Robertson and J. G. White.

The crystal and molecular structure of the orthorhombic modification of 1 : 2 : 5 : 6-dibenzanthracene has been determined by quantitative *X*-ray analysis. The molecular arrangement in the crystal is quite different from that found for other aromatic hydrocarbons (*e.g.*, anthracene, coronene, or pyrene). There are four molecules in the unit cell and these each possess an exact centre of symmetry (space-group *Pcab*). The molecules lie approximately in layers along the 200 planes, to which they are tilted at an angle of about 31°; 9 out of the 11 carbon atoms are separately resolved in the Fourier maps, and the bond lengths connecting these atoms can be directly measured. These vary from 1·38 to 1·45 A.

An approximate calculation of the bond distances from the 12 stable valency-bond structures for dibenzanthracene is given, but there is less agreement with the observed values than was found in coronene and pyrene.

Unfortunately, the accuracy is not likely to be quite as high as in the other structures mentioned above. In the central ring of the molecule the resolution is good and here the error should not exceed ± 0·02 A. In the outer parts of the molecule the bond-length variations (Fig. 3) must be considered rather doubtful. It is shown, however, that the co-ordinates given lead to better structure factor agreements than can be obtained from any regularised model.

Recent *X*-ray measurements on coronene and pyrene (Robertson and White, *J.*, 1945, 607; this vol., p. 358) have established that the carbon–carbon bond lengths vary slightly in different parts of these molecules. These variations are small, in fact, not much greater than the possible experimental error under present conditions; nevertheless, the variations do seem to conform to a fairly definite pattern which is capable of at least partial explanation in terms of the more important structures which contribute to the normal states of these molecules.

We have now extended our measurements to 1 : 2 : 5 : 6-dibenzanthracene. This hydrocarbon exists in two distinct crystalline modifications, monoclinic and orthorhombic. Preliminary data for the monoclinic form have been given by Iball and Robertson (*Nature*, 1933, **132**, 750). The orthorhombic form, with which we are concerned in the present paper, was first described by Krishnan and Banerjee (*Z. Krist.*, 1935, **91**, 170, 173), who studied the magnetic anisotropy of the crystal and from their measurements of the magnetic susceptibilities were able to deduce the approximate orientation of the molecules. Accurate values for the cell dimensions, and a determination of the space-group have been given by Iball (*Nature*, 1936, **137**, 361), but detailed atomic positions have not been given by any of these authors.

The crystal structure and molecular arrangement in orthorhombic dibenzanthracene differs from that of both the coronene and the pyrene structures. Like coronene, the molecules are found to display an exact centre of symmetry and to this extent the analysis is simplified. However, the unit cell contains four complete molecules and their mutual arrangement (see Figs. 1 and 2) makes it impossible to obtain resolution of all the atoms in any projection of the structures. In this respect the results obtained from the present two-dimensional analysis resemble the pyrene results, and they should similarly be regarded as a preliminary analysis, carried out with as much accuracy as possible, which must be undertaken before any further refinement by more elaborate three-dimensional methods can be attempted. In the present case the most favourable Fourier projection of the structure (Fig. 1) shows separate resolution of nine out of the eleven crystallographically independent carbon atoms, and direct measurements of these positions can be made. The results indicate certain bond-length variations, as shown in Fig. 3. These figures represent the most probable values, but they are unfortunately subject to certain errors. The accuracy in the central ring should be reasonably high, the errors here probably not exceeding ± 0·02 A. In the other parts of the molecule the observed bond-length variations must be considered rather doubtful.

Description of the Structure.—Crystal data. 1 : 2 : 5 : 6-Dibenzanthracene, $C_{22}H_{14}$; M, 278·3; m. p. 267·5°; d, calc. 1·294, found 1·282; orthorhombic bipyramidal, $a = 8·22$, $b = 11·39$, $c = 15·14$ A. (Iball). Absent spectra, ($0kl$) when l is odd, ($h0l$) when h is odd, ($hk0$) when h is odd. Space-group D_{2h}^{15} (or O_h^{15}) (*Pcab*). Four molecules per unit cell. Molecular symmetry, centre. Volume of the unit cell, 1418 A.^{3}. Absorption coefficient for *X*-rays, $\lambda = 1·54$ A., $\mu = 6·78$ cm.$^{-1}$; $\lambda = 0·71$ A., $\mu = 0·86$ cm.$^{-1}$. Total number of electrons per unit cell = F (000) = 584.

Structure analysis. The space-group *Pcab* with only four molecules in the unit cell requires that the molecules must possess centres of symmetry which coincide with the crystallographic centres of symmetry. The asymmetric unit may therefore be taken as one half of the chemical

FIG. 1(*a*).

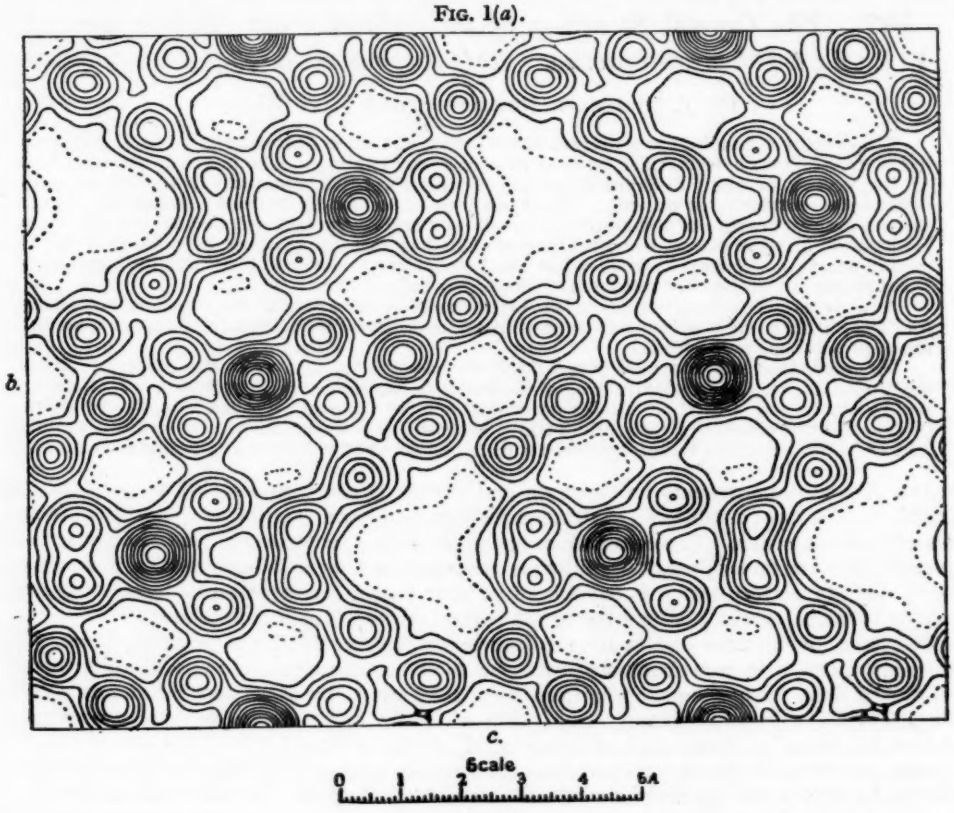
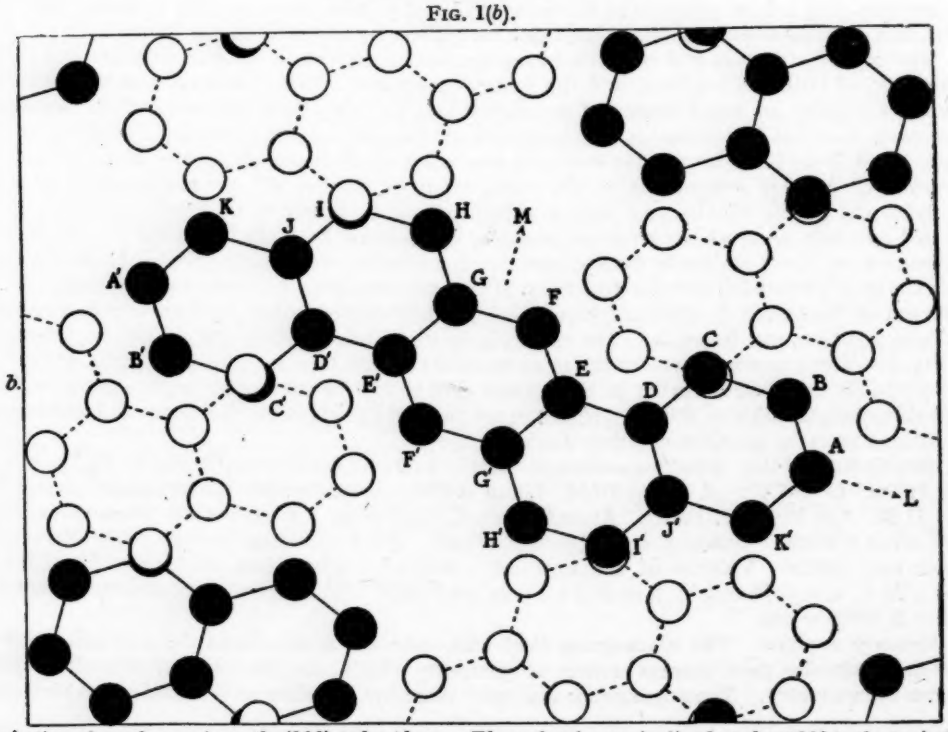


FIG. 1(*b*).



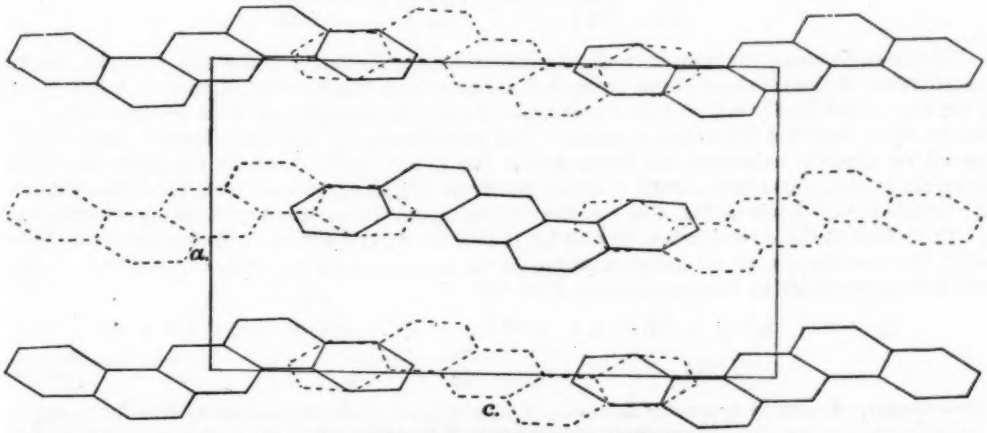
Projection along the a *axis on the* (100) *or* bc *plane. The molecules are inclined at about* 31° *to the projection plane. Each contour line corresponds to a density increment of one electron per* A.^{2}, *the one-electron line being dotted.*

molecule, or eleven carbon atoms, if we neglect the hydrogen atoms. As a first approximation a regular planar structure was assumed, according to the usual chemical formula.

The magnetic measurements of Krishnan and Banerjee (*loc. cit.*) give the tilt of the molecular plane to the *bc* plane as 29°, and these authors predict that the long axis of the molecule (*L* in Fig. 1*b*) probably lies along the *c* axis of the crystal. The first of these observations is probably fairly accurate, but the second can only be an approximation. Now, the strength of the (200) reflection (F = 153) suggests that if the molecular plane is inclined at about 30° to the *bc* plane, as the magnetic measurements suggest, then the line of zero tilt in the molecule must be its longest axis, that is, the molecular axis *L* must lie in, or very nearly in, the *bc* plane.

Bearing these factors in mind, only one degree of freedom remains to be fixed, the angle which *L* makes in the *bc* projections with the crystal axis *c* (or *b*). A suitably drawn projection of the molecules may then be pivoted about the centre of symmetry in the *bc* plane and the effect of various positions on the (0*kl*) structure factors may be tested by inspection or simple calculation. In practice the (020) structure factor was used as an index, as its low value (F = 24) makes it extremely sensitive. When the molecular axis *L* is made to coincide with the crystal axis *c* the calculated value of this structure factor is much too large, but it can be brought to the correct value by a rotation of about 16° away from the *c* direction. A further small rotation would make

FIG. 2.



View of the molecular arrangement projected on the 010 *plane. The dotted molecules are situated half a translation along the* b *axis.*

this structure factor pass through zero and assume a negative value, but this possibility can be ruled out by the calculation of certain other structure factors.

Detailed calculations on this basis gave reasonably good agreements between the measured and the calculated values of all the structure factors, and it was possible to proceed immediately to further refinement of the atomic positions by Fourier series methods. Two successive Fourier syntheses of the (0*kl*) zone were carried out, 50 terms being included in the first, and 56, all the reflections which could be observed in this zone, in the second. The results of this final synthesis are given by the contour map of Fig. 1(*a*), from which it can be seen that nine out of the eleven crystallographically independent atoms are resolved. The other two atoms, *C* and *I*, are obscured by the overlapping of related atoms in adjoining molecules as indicated in Fig. 1(*b*).

The *y* and *z* co-ordinates finally adopted were obtained from those actually measured on this map after a correction for incompleteness of the Fourier series due to Booth (*Nature*, 1945, **156**, 51). In this method a Fourier synthesis of the same zone is carried out using the calculated instead of the observed values of the structure factors and omitting all terms which are omitted in the final Fourier synthesis. The resulting map was found to give certain small changes in the atomic positions and these shifts were added to the observed co-ordinates but with opposite sign. This led to a slight improvement in the agreements between the measured and the calculated values of the structure factors, as described below (Experimental Section).

The *x* co-ordinates of the atoms cannot be obtained directly, as the other possible projections would give little information because of overlapping effects. These co-ordinates can only be calculated on the assumption that the molecule is planar, but this assumption is well supported

by the agreements obtained between the calculated and the observed values of the structure factors for the other two zones.

A complete picture of the crystal symmetry may be obtained by considering Fig. 1 in conjunction with Fig. 2, which shows diagrammatically the projection along the *b* axis.

Orientation, co-ordinates, and dimensions. By assuming a planar molecule and averaging certain distances as described more fully in the Experimental Section, it is possible to calculate the orientation of the molecule. The results are given in Table I, where χ, ψ, and ω are the angles which the molecular axes *L* and *M* [Fig. 1 (*b*)] and their perpendicular, *N*, make with the *a*, *b*, and *c* crystallographic axes. These results give the inclination of the molecular plane to the (100) plane, expressed by χ_N, as 31·3° in reasonably good agreement with the value of 29° predicted by Krishnan and Banerjee (*loc. cit.*).

TABLE I.

Orientation of the molecule in the crystal.

$\chi_L = 92{\cdot}1°$	$\cos\chi_L = -0{\cdot}0374$	$\chi_M = 58{\cdot}8°$	$\cos\chi_M = 0{\cdot}5180$
$\psi_L = 106{\cdot}1°$	$\cos\psi_L = -0{\cdot}2771$	$\psi_M = 35{\cdot}3°$	$\cos\psi_M = 0{\cdot}8162$
$\omega_L = -16{\cdot}2°$	$\cos\omega_L = 0{\cdot}9601$	$\omega_M = 75{\cdot}2°$	$\cos\omega_M = 0{\cdot}2558$
	$\chi_N = 31{\cdot}3°$	$\cos\chi_N = 0{\cdot}8545$	
	$\psi_N = 120{\cdot}5°$	$\cos\psi_N = -0{\cdot}5069$	
	$\omega_N = 96{\cdot}5°$	$\cos\omega_N = -0{\cdot}1130$	

The co-ordinates with respect to the crystal axes are collected in Table II; y_1 and z_1 are the co-ordinates of the resolved atoms measured directly from the Fourier projection, while y_2 and z_2 are the values finally adopted after correction for the incompleteness of the Fourier series. It will be seen that the difference is small. The co-ordinates of the two atoms *C* and *I* which cannot be directly measured are those which the atoms would have in a regular hexagonal molecule in the above orientation. These positions are in agreement with the appearance of the double peaks shown in Fig. 1(*a*) but the centres cannot be assigned with any great certainty.

Table II lists the co-ordinates (*x*, *y*, *z*) for the eleven carbon atoms in the asymmetric crystal unit; the co-ordinates of all the other atoms in the unit cell may be obtained from these by the relations appropriate to the space-group *Pcab*, *viz.*,

$$\pm\,(x, y, z;\ 1/2 + x, 1/2 - y, z;\ x, 1/2 + y, 1/2 - z;\ 1/2 - x, y, 1/2 + z)$$

TABLE II.

Co-ordinates. Centre of symmetry as origin; y_1 and z_1 are co-ordinates measured directly, y_2 and z_2 co-ordinates adopted after correction.

Atoms [cf. Fig. 1(*b*)].	*x*, A.	y_1, A.	y_2, A.	z_1, A.	z_2, A.	$2\pi x/a$.	$2\pi y_2/b$.	$2\pi z_2/c$.
A	−0·215	−1·580	−1·584	5·465	5·476	− 9·4°	−50·1°	130·3°
B	0·444	−0·380	−0·392	5·094	5·108	19·4	−12·4	121·4
C	0·504	0·020	0·020	3·723	3·723	22·1	0·6	88·5
D	−0·095	−0·776	−0·770	2·738	2·740	− 4·2	−24·3	65·1
E	−0·028	−0·370	−0·354	1·382	1·392	− 1·2	−11·2	33·2
F	0·600	0·786	0·794	0·992	0·978	26·2	25·0	23·3
G	0·647	1·198	1·172	−0·384	−0·376	28·3	37·1	− 8·9
H	1·328	2·404	2·404	−0·760	−0·740	58·2	76·0	− 17·6
I	1·381	2·794	2·794	−2·097	−2·097	60·5	88·3	− 49·8
J	0·769	1·980	1·978	−3·076	−3·063	33·7	62·6	− 73·0
K	0·827	2·380	2·388	−4·452	−4·448	36·2	75·3	−105·9

The molecular dimensions and bond lengths may be calculated from these co-ordinates and are shown graphically in Fig. 3. The ringed atoms are those separately resolved in Fig. 1, and the bond distances between these atoms are the only ones which can be obtained directly.

From the orientation of the molecule and the co-ordinates given in Table II the molecular co-ordinates of the atoms may be calculated and these are collected in Table III.

Intermolecular distances. The closest distance of approach between atoms of different molecules occurs between the standard molecule and the reflected molecule at $(1/2 - x, y, 1/2 + z)$. Between *C* on the standard molecule and *J* on this reflected molecule the distance is 3·54 A., while between *F* and *A'* the atoms are 3·56 A. apart. Other distances in this direction are *CD'* 3·76 A., *CK* 3·71 A., *EB'* 3·87 A., and *FK* 3·78 A. The distances are not quite so close between the first molecule and the reflected molecule at $1/2 + x$, $1/2 - y$, z, where the atom *I* on the standard molecule is 3·59 A. from *D'* on the reflected molecule, 3·75 A. from *J*, and 3·82 A.

TABLE III.

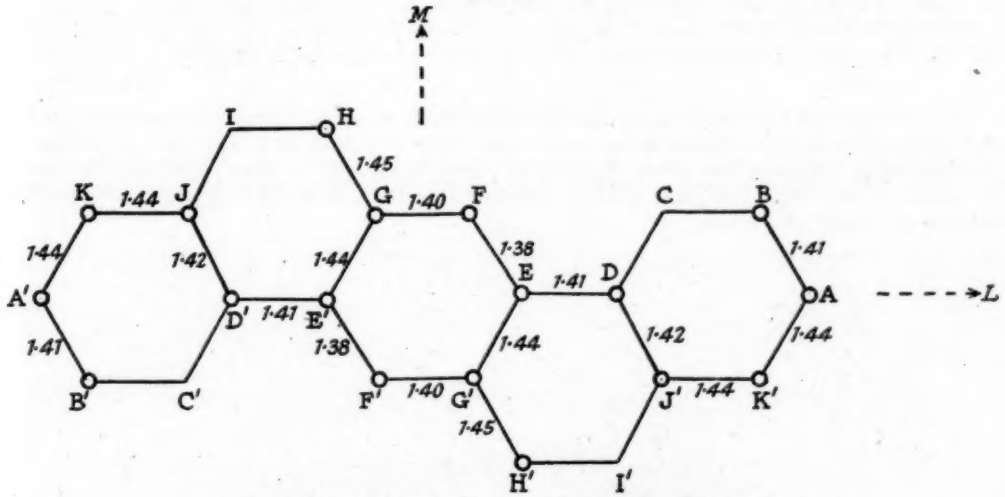
Co-ordinates with respect to molecular axes.

Atom.	*L*, A.	*M*, A.	*N*, A.	Atom.	*L*, A.	*M*, A.	*N*, A.
A	5·703	−0·003	0	*G*	−0·708	1·196	0
B	4·996	1·218	0	*H*	−1·427	2·460	0
C	3·550	1·230	0	*I*	−2·840	2·460	0
D	2·847	0·023	0	*J*	−3·520	1·229	0
E	1·435	0·050	0	*K*	−4·964	1·240	0
F	0·696	1·209	0				

from *E'*. All other pairs of atoms are more than 4 A. apart, and the distances given above are just about the same as the usual intermolecular distances encountered in hydrocarbon structures.

It will be noted that in the dibenzanthracene structures all the primitive translations are greater than 8 A., and we do not encounter pairs of molecules which directly overlie one another as in the phthalocyanine, coronene, or pyrene structures. It is therefore not profitable to discuss the normal projections of pairs of parallel molecules in this case, because they are widely separated and interleaved with parts of other differently oriented molecules.

FIG. 3.



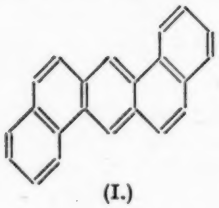
Dimensions of the molecule of 1 : 2 : 5 : 6-*dibenzanthracene.*

Discussion of Results.—The bond-length measurements given in Fig. 3 vary from 1·38 to 1·45 A., a slightly larger range than that found in coronene, and about the same as that found in pyrene (Robertson and White, *loc. cit.*). Unfortunately, the accuracy obtained in the present investigation is not likely to be quite as high as in these other structures. The unusually large values found for *GH*, *JK*, and *KA'* are very difficult to assess, as the atoms *H* and *K* are so distorted by their proximity to the corresponding atoms in the reflected molecule that their centres are rather more uncertain than those of the other resolved atoms. These bond lengths must therefore be considered as rather doubtful. The central ring, however, is quite free from any such distorting effects, and here the maximum error in the bond lengths should not be greater than ± 0·03 A., and probably does not exceed ± 0·02 A. The bond *GE* is, therefore, probably longer than the other two independent bonds in this ring, which are both very close to the benzene value of 1·39 A.

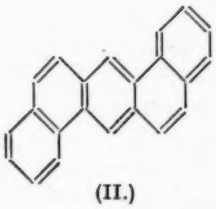
Beyond this fairly definite conclusion little can be said with certainty. It will be noted that the dibenzanthracene molecule contains no symmetry element apart from the centre that can be used to average the bond lengths into any system of groups, as was done for coronene. However, the measurements recorded in Fig. 3 do receive a measure of general support from the very satisfactory agreements obtained between the observed and calculated values of the structure factors (Table IV). These agreements are better than can be obtained from any regular model placed in the same orientation.

For comparison with the results obtained for coronene and pyrene (Robertson and White,

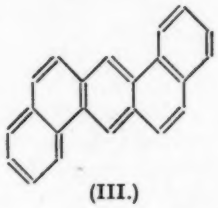
loc. cit.) we give below the calculated values of the bond lengths worked out on the same basis as in the previous papers. In this calculation the 12 stable valency bond structures for 1 : 2 : 5 : 6-dibenzanthracene, (I)—(VI) and six other structures derived from these by inversion through the centre of symmetry, are regarded as making equal contributions to the normal state of the molecule.



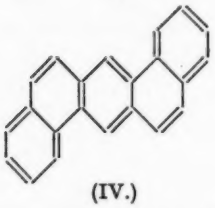
(I.)



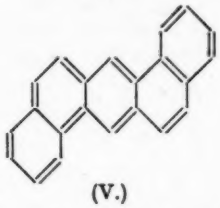
(II.)



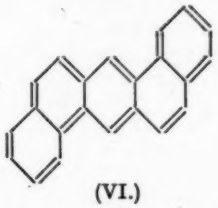
(III.)



(IV.)

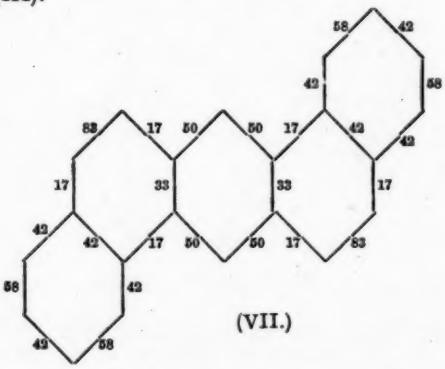


(V.)

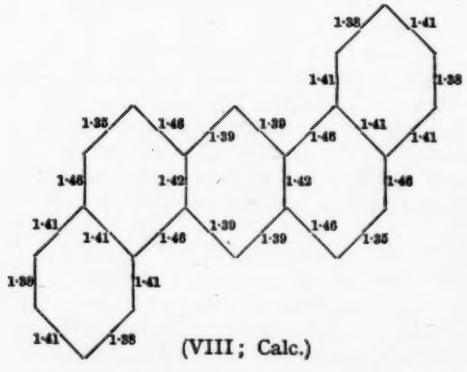


(VI.)

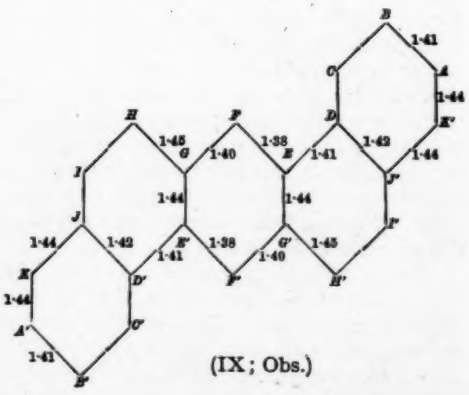
By counting the number of times that any given bond is a double bond, we may compute the percentage double-bond character for each link. This is shown in (VII), and in (VIII) the corresponding distances are given, as derived from the empirical Pauling–Brockway curve (*J. Amer. Chem. Soc.*, 1937, **59**, 1223). The measured values as derived from the present analysis are repeated in (IX).



(VII.)



(VIII; Calc.)



(IX; Obs.)

It will be noted that in the central ring there is a rather striking qualitative resemblance between the calculated and the observed values. In the rest of the molecule, however, there

is little agreement. The widest divergence is in the bond $K'A$, which is calculated as rather shorter than the benzene value and found experimentally longer than the graphite distance. As stated above, the position of K is rather uncertain, and under such conditions agreement could not be expected.

Structures (I) and (II) each contain four benzenoid rings, (III) and (IV) each contain three, and (V) and (VI) each contain only two, the remaining rings being quinonoid in type. If we attempt to apply the Fries rule, by preferring those structures which contain the largest number of benzenoid rings, the effect on the above calculations is disappointing. The bond lengths in the central ring tend to become equalised at the benzene value of 1·39 A., and in the other parts of the molecule more extreme values are obtained, which are not in agreement with the observations.

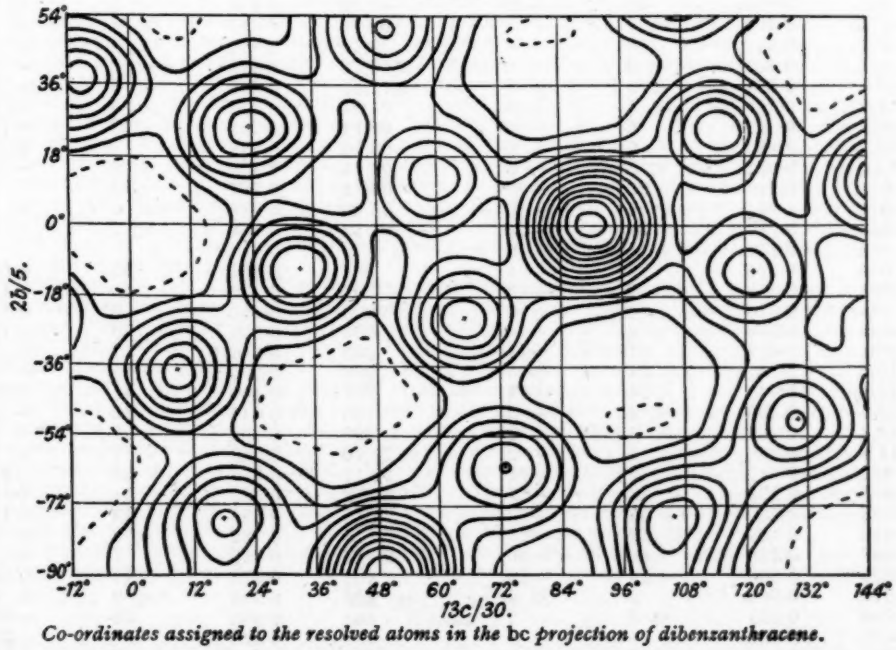
While lack of agreement in the outlying parts of the molecule may be due to experimental error to some extent, it should be noted that no rigorous theoretical derivation of bond lengths in a molecule of this shape has yet been made. It is possible that the excited structures (completely neglected in the above treatments) may play an appreciable part in such an asymmetric molecule, while in more symmetric molecules of the coronene type they may be relatively less important.

The calculated average value for the bond lengths in (VIII) is 1·41 A., while the experimental average is 1·42 A. The latter figure is, surprisingly, rather larger than that usually found in polycyclic aromatic hydrocarbons. It would, however, be necessary to determine the primitive translations of the crystal with greater accuracy before attaching undue importance to this average figure.

Experimental.

X-Ray Measurements.—Most of the *X*-ray work was carried out photographically with Cu-$K\alpha$ radiation ($\lambda = 1{\cdot}54$), using rotation, oscillation, and moving-film methods. In addition, certain absolute measurements were made on the ionisation spectrometer, using monochromatic copper and molybdenum radiation.

Fig. 4.



Co-ordinates assigned to the resolved atoms in the bc *projection of dibenzanthracene.*

Some very beautifully formed specimens of the crystals were supplied by Dr. Iball, crystallised from ethyl acetate. These crystals appear to be remarkably stable and are little affected by exposure to *X*-rays; we have used some of them for many years as sub-standards for calibration purposes in absolute intensity work.

For the present investigation the intensity work was carried out mainly on three different specimens, which weighed 0·116, 0·081, and 0·0665 mg., respectively. These specimens were selected so that on rotation the path of the *X*-ray beam in the crystal did not vary by more than about 0·2 mm., and relative

TABLE IV.

Measured and calculated values of the structure factor.

hkl.	sin θ ($\lambda = 1{\cdot}54$).	F, meas.	F, calc.	*hkl.*	sin θ ($\lambda = 1{\cdot}54$).	F, meas.	F, calc.
002	0·102	50	−49	048	0·488	7	+ 4
004	0·203	13	−14	058	0·529	5	+ 8
006	0·303	10	+16	068	0·574	8	+12
008	0·407	30	−27	078	0·624	28	−27
00,10	0·508	16	−19	088	0·677	34	+31
00,12	0·610	< 5	− 6	098	0·731	13	−14
00,14	0·711	< 5	+ 3	0,10,8	0·789	< 5	0
00,16	0·812	< 4	+ 2	0,11,8	0·848	< 4	0
00,18	0·916	< 3	− 3	0,12,8	0·906	< 3	− 3
				0,13,8	0·968	< 2	− 2
020	0·135	24	+34	01,10	0·510	8	+ 7
040	0·270	55	+50	02,10	0·524	7	− 6
060	0·406	10	− 7	03,10	0·545	4	+ 2
080	0·541	15	− 6	04,10	0·573	6	−11
0,10,0	0·676	< 5	0	05,10	0·608	< 5	+ 8
0,12,0	0·810	< 4	− 1	06,10	0·648	< 5	+ 5
0,14,0	0·946	< 3	+ 2	07,10	0·693	6	− 6
				08,10	0·740	9	−11
200	0·188	153	+170	09,10	0·793	< 5	0
400	0·375	7	− 5	0,10,10	0·847	< 4	+ 1
600	0·562	< 5	− 3	0,11,10	0·901	< 4	0
800	0·749	5	− 8	0,12,10	0·957	< 3	− 2
				01,12	0·611	8	+ 7
012	0·122	28	+35	02,12	0·623	31	+42
022	0·169	4	− 2	03,12	0·641	27	+32
032	0·227	43	−36	04,12	0·665	9	+ 9
042	0·289	40	−38	05,12	0·696	< 5	+ 1
052	0·354	37	+30	06,12	0·731	4	+ 3
062	0·419	45	−43	07,12	0·712	< 5	+ 4
072	0·484	< 4	− 7	08,12	0·815	< 4	+ 2
082	0·551	< 4	− 1	09,12	0·861	< 4	− 1
092	0·617	< 5	− 2	0,10,12	0·910	< 3	− 2
0,10,2	0·684	< 5	+ 2	0,11,12	0·962	< 3	− 1
0,11,2	0·750	< 5	− 3	01,14	0·712	< 5	− 2
0,12,2	0·817	5	− 5	02,14	0·721	13	−14
0,13,2	0·883	6	+ 6	03,14	0·738	8	+ 8
0,14,2	0·952	< 3	− 3	04,14	0·760	< 5	− 3
014	0·214	26	+22	05,14	0·787	< 5	0
024	0·244	4	+ 5	06,14	0·818	< 4	− 1
034	0·287	34	−29	07,14	0·854	< 4	− 4
044	0·338	4	− 5				
054	0·394	6	+ 4	201	0·194	52	+54
064	0·454	7	+13	202	0·212	50	−41
074	0·515	4	+ 4	203	0·240	9	+11
084	0·578	< 4	− 5	204	0·275	10	−13
094	0·642	11	+11	205	0·314	7	− 5
0,10,4	0·707	24	+23	206	0·356	< 5	+ 5
0,11,4	0·772	26	+23	207	0·400	41	+36
0,12,4	0·835	< 4	+ 3	208	0·446	18	−12
0,13,4	0·901	< 4	− 2	209	0·492	< 7	+ 3
0,14,4	0·968	< 2	+ 2	20,10	0·539	< 7	+ 5
016	0·311	19	+23	20,11	0·587	30	+37
026	0·333	35	−27	20,12	0·635	14	+14
036	0·366	36	+33	20,13	0·684	13	−14
046	0·407	29	−28	20,14	0·732	< 8	+ 4
056	0·456	40	−40	20,15	0·786	7	+ 5
066	0·508	19	−19	401	0·378	17	−18
076	0·563	5	+ 6	402	0·388	< 6	+ 4
086	0·621	< 5	− 2	403	0·405	23	−20
096	0·681	6	− 4	404	0·426	36	−37
0,10,6	0·740	4	− 7	405	0·453	9	−12
0,11,6	0·795	< 5	−12	406	0·482	7	+ 2
0,12,6	0·867	< 4	− 1	407	0·516	14	+10
0,13,6	0·930	< 3	− 1	408	0·551	< 7	+ 8
0,14,6	0·994	< 2	− 2	409	0·590	15	−13
018	0·410	20	+21	40,10	0·630	< 8	+ 1
028	0·427	< 3	+ 2	40,11	0·671	28	+29
038	0·454	21	−25	40,12	0·714	15	+16

TABLE IV.—*continued.*

Measured and calculated values of the structure factor.

hkl.	sin θ (λ = 1·54).	F, meas.	F, calc.	*hkl.*	sin θ (λ = 1·54).	F, meas.	F, calc.
40,13	0·760	< 8	+ 1	260	0·448	13	+ 15
40,14	0·800	< 8	− 6	280	0·574	13	− 7
40,15	0·853	10	+ 6	2,10,0	0·703	< 9	− 3
601	0·565	12	−14	320	0·312	76	− 76
602	0·570	10	+10	340	0·389	16	+ 15
603	0·582	9	+11	360	0·494	< 7	− 2
604	0·597	39	−31	380	0·610	19	+ 15
605	0·616	8	− 9	3,10,0	0·733	16	+ 7
606	0·638	< 8	+ 3	420	0·399	60	+ 60
607	0·664	< 8	− 2	440	0·463	10	− 9
608	0·691	< 8	+ 4	460	0·553	9	+ 5
609	0·722	< 8	+ 3	480	0·659	< 8	+ 2
801	0·753	< 8	0	4,10,0	0·773	15	− 9
802	0·760	< 8	− 2	520	0·487	20	− 19
803	0·766	16	+12	540	0·541	< 8	− 12
804	0·780	10	− 5	560	0·620	16	+ 16
				580	0·716	< 9	0
120	0·165	71	− 71	5,10,0	0·823	11	+ 7
140	0·287	36	+ 34	620	0·578	9	− 10
160	0·417	17	− 20	640	0·624	14	+ 11
180	0·549	21	+ 19	660	0·693	7	− 7
1,10,0	0·682	< 8	0	680	0·780	< 8	+ 4
220	0·232	108	+108	720	0·670	< 8	0
204	0·330	10	− 8	740	0·710	< 9	− 2

absorption corrections for different reflections in the same zone were neglected. Most of the intensities were measured from calibrated films, using an integrating photometer of the type described by Robinson (*J. Sci. Instr.*, 1933, **10**, 233). Only a few of the weakest reflections were estimated visually.

The absolute measurements were made directly on the ionisation spectrometer, with monochromatic rays, and also by means of sub-standards, employing the photographic technique (Robertson, *ibid.*, 1943, **20**, 175). The usual formulæ and correction factors for mosaic crystal specimens were employed.

Fourier Analysis.—Using the phase constants obtained initially from the trial structures and the measured values of F, a double Fourier series was set up according to the usual formulæ. The electron density was computed at 450 points on the asymmetric unit, the *b* axis being divided into 60 parts (intervals of 0·190 A.) and the *c* axis into 60 parts (intervals of 0·252 A.). The summations were carried out by means of three-figure strips (Robertson, *Phil. Mag.*, 1936, **21**, 176). The positions of the contour lines were obtained by graphical interpolation from the summation totals, by making sections of both the rows and columns. The resulting contour map is shown in Fig. 1, the whole unit cell being included.

Orientation of the molecule and co-ordinates. From an inspection of the observed lengths in projection of *ED* and parallel distances, which can be only very slightly tilted, it was found that the best average radius of the hexagons is 1·42 A. With this average value and the assumptions that *L* and *M* are at right angles and that the molecule is planar, it was possible to calculate the orientation of the molecule with respect to the crystallographic axes.

The distances *FG'*, *EH'*, and *BK'* as measured from the projection given in Fig. 1 are 2·102 ± 0·040 A., and from the assumed mean radius of the hexagons (1·42 A.) the angle χ_M which *M* makes with the *a* crystal axis is obtained as 58·8°. The inclination of *L* cannot be derived in this way because it is very near to 90°. The calculation may, however, be made from the observed angle between *L* and *M* in the projection. The projected lines *ADE*, *BF*, and *K'J'G'* are inclined at a mean angle of − 16·1° ± 0·6° to the *c* axis, and the lines *BK'*, *EH'*, and *FG'* make the mean angle of 72·6° ± 0·3° with *c*. From these figures the complete orientation of the assumed regular planar molecule may be obtained by relations similar to those already given for the coronene analysis (Robertson and White, *loc. cit.*).

The next step consists of assigning the most probable positions to the centres of the resolved atoms, without the aid of any regularised model. The positions finally adopted after the Booth corrections for incompleteness of the Fourier series, etc., are shown by small crosses in Fig. 4. From these positions and the orientation now calculated, the actual molecular co-ordinates may be obtained (Table III), and the interatomic distances readily follow. The crystal co-ordinates are given in Table II.

The structure factors of the (0*kl*) zone have been recalculated on various assumptions, and the mean discrepancy, expressed as

$$\frac{\Sigma\{|F_{meas.}| - |F_{calc.}|\}}{\Sigma F_{meas.}}$$

has been evaluated with the following results. For a regular hexagonal model with a constant carbon–carbon distance of 1·42 A. placed in the best orientation, the discrepancy is 16·1%. For the co-ordinates obtained directly from the contour maps (Figs. 1 and 4) without any assumptions about regularity (y_1, z_1 in Table II), the discrepancy is reduced to 15·0%. After the Booth corrections, the final values for the co-ordinates, which are used for calculating the bond lengths (y_2, z_2 in Table II), give a discrepancy of 13·8%. The differences between these figures are small, and their significance is difficult to estimate, but they do seem to justify the use of our final co-ordinates as being preferable to any set of regularised co-ordinates.

In calculating the structure factors the scattering curve formerly used for hydrocarbons (Robertson, *Proc. Roy. Soc.*, 1935, *A*, **150**, 110) was found to be rather unsuitable, as the calculated values for small spacing planes were consistently higher than the observed values. For the large spacing planes the tendency was for the observed structure factors to be larger than the calculated. In order to keep the upper part of the scattering curve at the usual values, all the absolute F's were multiplied by a scale correction factor of 0·84 and then an empirical scattering curve was drawn for sin $\theta = 0{\cdot}5$—$0{\cdot}9$. The values used for this range are given below (max. $f_e = 100$).

sin θ ($\lambda = 1{\cdot}54$)	0·5	0·6	0·7	0·8	0·9
f_e	23·5	15·0	9·5	7·0	4·5

The general agreements calculated from the final co-ordinates are quite as good as are usually found in this type of analysis. The discrepancies are 13·8% for the ($0kl$) zone, 12·0% for the ($hk0$) zone, and 13·2% for the ($h0l$) zone. For all structure factors the mean discrepancy is 12·6%. The measured and calculated values of the structure factors are collected in Table IV.

We thank Professor J. W. Cook, F.R.S., and Dr. J. Iball for pure specimens of material used in this work, and Dr. Iball for much valuable preliminary data. We are also indebted to the Royal Society for a grant which defrayed the cost of some of the apparatus employed.

UNIVERSITY OF GLASGOW. [*Received, November 4th*, 1946.]

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188. *The Chemistry of Plutonium.*

By B. G. HARVEY, H. G. HEAL, A. G. MADDOCK, and (MISS) E. L. ROWLEY.

A survey of some of the chemical and electrochemical properties of plutonium has been made. Valency states of 3, 4, and 6 have been established.

Oxidation and reduction reactions between the different valency states have been investigated. The reactions of plutonium ions with some of the commoner organic reagents are described.

PLUTONIUM was discovered late in 1940 by Seaborg, McMillan, Kennedy, and Wahl (*Physical Rev.*, 1946, **69**, 366; see also Seaborg, Wahl, and Kennedy, *ibid.*, p. 367). The investigations now reported were carried out with about 5 mg. of ^{239}Pu extracted from neutron-irradiated uranium. Experiments were carried out either with the plutonium in tracer concentrations, or else, by microchemical methods, with plutonium concentrations of the order of 1 mg. per ml. ^{239}Pu is an α-active nucleus with a half-life of $2{\cdot}4 \times 10^4$ years (Seaborg, *Chem. Eng. News*, 1945, **23**, 2190).

I. *The Valencies of Plutonium.*—Plutonium was investigated in each of three well-defined valency states. It appears to be more stable to both mild oxidation and reduction when it is in the middle valency state of the three; in this condition, it was shown to be quadrivalent (see Experimental, A).

Polarographic experiments in plutonium solutions showed the presence of a wave at a half-wave potential of + 0·7 volt on the hydrogen scale. It was already known that plutonium could be oxidised to a valency state higher than 4, but the observed wave did not appear to be sufficiently positive to correspond to this process. It was therefore suspected that the wave corresponded to the reduction of plutonium to a state with a valency lower than 4. The existence of such a state was immediately confirmed chemically, and its valency was shown to be 3 by two methods (Experimental, B, i and ii), and that of plutonium in its highest oxidation state was shown to be 6 by the experiment described under B, iii.

II. *The Electrochemistry of Plutonium.*—Plutonium, like uranium, is a base metal and a transition element. Electrochemical studies were therefore mainly concerned with the processes of oxidation and reduction between the various valency states, and with complex formation. Evidence for complex formation is presented elsewhere (Sect. IV).

The potential of the Pu–Pu(III) *couple.* No indication of the potential of this couple has been obtained. The corresponding couple U–U(III) has a potential which has been estimated at − 1·5 volts (European sign convention) (Heal, unpublished work), and it is probable that the value for plutonium is not very different from this.

The potential of the couple Pu(III)–Pu(IV). The potential was determined both by direct measurement and polarographically (see C and D). The best characterised waves obtained are shown in Figs. 3*a*, 3*b*, and 3*c*. In all cases the diffusion current was lower for Pu(IV) than for Pu(III) solutions. The explanation of this phenomenon remains obscure.

The estimates of the molal oxidation–reduction potential given below were taken from the

direct determination in the case of sulphuric acid, and from the half-wave potentials in the other two cases:

In 1N-H_2SO_4, + 0·72 volt at 23°. In 1N-HCl, + 0·99 volt at 30°. In 1N-$HClO_4$, + 0·86 volt at 23°.

These results show that the tervalent plutonium ion is a much less powerful reducing agent than the tervalent uranium ion (which liberates hydrogen from water). Indeed, the quadrivalent plutonium ion may be reduced to the tervalent state by the quadrivalent uranium ion. This reaction was studied polarographically at 30°, with the results recorded in E (Experimental).

III. *The Reactions of Plutonium.*—(a) *Oxidation–reduction reactions.* (i) In aqueous solutions, Pu(IV) may be reduced to Pu(III) by sulphur dioxide, hydroxylamine hydrochloride, the uranous ion, hydrazine hydrochloride, the iodide ion, electrolytically at a platinum cathode, or by shaking with mercury in chloride solutions.

The reaction with sulphur dioxide is slow at room temperature, but in hot solutions it goes to completion in about 5 minutes. The reduction of Pu(IV) by the iodide ion is also somewhat slow at room temperature in both sulphate and chloride solutions. The titration of the liberated iodine does not appear to be a useful method for the routine determination of plutonium.

(ii) Oxidation of Pu(III) by atmospheric oxygen is fairly rapid, and solutions of Pu(III) salts are completely oxidised to Pu(IV) on two or three evaporations to dryness in an open vessel in air. However, Pu(III) solutions are stable in an inert atmosphere. Permanganate oxidises Pu(III) quantitatively to Pu(IV) at room temperature in acid solutions. At 60°, the plutonium is oxidised to the sexavalent state.

(iii) In tracer concentrations of plutonium, the following oxidising agents were found to oxidise the Pu(IV) ion to the sexavalent state: hot potassium permanganate, potassium dichromate, argentic salts (including sodium perdisulphate in the presence of silver ions), and ceric ions. The conditions found to give satisfactory oxidation with perdisulphate and silver ions in these experiments are set out in section F (Experimental).

In concentrations of about 1 mg. per ml., Pu(IV) was oxidised to the sexavalent state by the following reagents: potassium permanganate in hot acid solution, hot sodium perdisulphate, argentic nitrate at room temperature, or hot bromate solutions containing nitric acid.

(iv) Pu(VI) is reduced to the ter- or quadri-valent state by sulphur dioxide, ferrocyanide ions, and hydrogen peroxide. The last reaction is complicated by a subsequent reaction between the hydrogen peroxide and the Pu(IV) ion to give a precipitate of a plutonium peroxide (see p. 1012).

(b) *Compounds of tervalent plutonium.* Solutions of tervalent plutonium salts are bright blue. The sulphate, chloride, and perchlorate are readily soluble in dilute acids. On addition of an excess of ammonium hydroxide a dirty blue precipitate of plutonium hydroxide is obtained. It may readily be redissolved in dilute acids to give solutions of Pu(III) salts.

The fluoride is insoluble in dilute acids, and tracer amounts of tervalent plutonium may be removed from solution by coprecipitation with lanthanum fluoride in the presence of hydrofluoric acid.

In the presence of hydroxylamine hydrochloride (to keep the plutonium in the reduced state), Pu(III) can be precipitated on a carrier of lanthanum oxalate. The removal of plutonium from the solution, however, was only 75% complete. The plutonium could be removed from the lanthanum oxalate carrier by washing with hot ammonium oxalate solution. It was not removed by ammonium oxalate solution at room temperature.

In acetate buffers at pH's of 3·6 and 5·6 it was found that Pu(IV) was much more completely removed from solution on a precipitate of bismuth oxychloride than was Pu(III); Pu(IV) ions therefore appear to be much more readily hydrolysed in solution than Pu(III) ions. To prevent losses of plutonium by adsorption on to glass, it is always necessary to work in acid solutions: pH < 1 is normally safe.

Pu(III) cannot be removed from acid solutions by coprecipitation with zirconium and one of the typical reagents for quadrivalent ions such as phenylarsonic acid or *m*-nitrobenzoic acid. Since Pu(IV) may readily be precipitated under these conditions, this enables a separation of Pu(III) from Pu(IV) to be carried out (see p. 1013).

(c) *Compounds of quadrivalent plutonium.* Solutions of the quadrivalent salts of plutonium are pale pink, with the exception of the nitrate, whose solutions are green.

Oxide, PuO_2. Ignition of the nitrate, iodate, or hydroxide of quadrivalent plutonium at about 500—600° yields a dark brown oxide PuO_2. In thin layers, the oxide appears to be yellow. If prepared by gentle ignition, it may easily be redissolved in hot concentrated

sulphuric or nitric acid. If ignited to a bright red heat, it dissolves readily only in potassium hydrogen sulphate at a dull red heat.

Hydroxide. The hydroxide is precipitated on the addition of ammonium hydroxide to solutions of Pu(IV) salts. It is a pale green gelatinous substance which can be centrifuged very readily. Precipitation of this hydroxide is one of the most convenient ways of removing plutonium from solution.

After being washed with dilute ammonium hydroxide and dried at 100°, the hydroxide dissolves readily in 1N-mineral acids, but decidedly more readily in nitric than in sulphuric or hydrochloric acid.

Peroxide. When hydrogen peroxide is added to an acid solution of a quadrivalent plutonium salt, a red-brown colour develops, and a bulky green precipitate of doubtful composition is slowly deposited. Precipitation of the plutonium is most complete in the pH range 3—4·5. The presence of sulphate ion appears to favour the reaction.

A precipitate of the same nature is obtained by adding hydrogen peroxide to solutions containing sexavalent plutonium, but it is formed less readily than from Pu(IV) solutions. It is therefore probable that the peroxide is a compound of quadrivalent plutonium, and that hydrogen peroxide reduces Pu(VI) to Pu(IV). The peroxide of plutonium is therefore quite different from uranium peroxide (peruranic acid). It is insoluble in sodium hydroxide solutions, and is presumably not a per-acid.

The peroxide dissolves in concentrated nitric acid with evolution of oxygen, to give a bright blue solution. When this solution is warmed, more oxygen is lost, and the blue solution fades to the pale green of Pu(IV) nitrate solutions. The peroxide may also be dissolved in 6% sulphurous acid solution.

The ratio of plutonium to peroxidic oxygen in the peroxide was determined by permanganate titration as described in the Experimental (G, i); if the permanganate reacted with the peroxidic oxygen in the same way as it does with hydrogen peroxide, the titration indicates that the ratio of atoms plutonium to atoms peroxidic oxygen is 2 to 3 (see G, ii). If the 0·335 mg. not accounted for is expressed as oxygen, the data give the following atomic ratios: Pu, 1; SO_4, 0·30; O (peroxidic and non-peroxidic), 2·93. The peroxide could therefore be written as $PuO_3,\frac{1}{3}SO_4$. It is possible that the dried peroxide is different in composition from the original precipitate. Thorium, for example, forms two peroxides, Th_2O_7 (or Th_2O_7,SO_4) and ThO_3. The latter form is more stable than the former, and is obtained when the former is allowed to decompose (Pascal, " Traité de Chimie Minérale," Vol. 11, p. 289).

Fluoride. The fluoride of Pu(IV) coprecipitates very well with lanthanum fluoride. Experiments (see H) were carried out to determine the weight of lanthanum which must be precipitated as fluoride in order to obtain efficient carrying of the plutonium. Precipitation of plutonium on a lanthanum fluoride carrier under these conditions appears to be substantially complete when the weight of lanthanum precipitated is greater than about 0·1 mg. per ml. of plutonium solution.

The precipitation of plutonium fluoride in the absence of a carrier was uncertain: 0·35 mg. of Pu(IV) in 2 ml. of 1N-perchloric acid was not precipitated by the addition of 48% hydrofluoric acid. In higher concentrations of plutonium, a gelatinous precipitate was obtained which quickly collapsed to a dense yellowish powder, difficult to centrifuge off on account of its lack of coherence. The precipitation of an equal weight of lanthanum fluoride was found to bind the precipitate and eliminate this difficulty.

Sulphate, $Pu(SO_4)_2$. Evaporation of Pu(IV) solutions, prepared from the hydroxide and sulphuric acid or from the peroxide and sulphurous acid in the presence of sulphuric acid, followed by gentle ignition to remove the sulphuric acid, gives anhydrous *plutonium sulphate* as a light pink powder. The same compound is obtained when the oxide PuO_2 is fumed down to dryness with sulphuric acid. The anydrous salt may be weighed in air. It is soluble in dilute mineral acids to give pale pink solutions. Dilute sulphuric acid solutions appear to be metastable, and sometimes a deposit of red-brown crystals is obtained on standing (Experimental, I).

Nitrate. Solutions of the nitrate in nitric acid are green. A sample of the hydrated solid nitrate was readily soluble in nitromethane.

Iodate, $Pu(IO_3)_4$. The iodate is obtained as a voluminous, very pale pink precipitate on addition of iodic acid or an iodate solution to solutions of Pu(IV) salts. It dissolves readily in 6% sulphurous acid solution, giving a solution containing tervalent plutonium.

Phenylarsonate. Pu(IV) is coprecipitated very efficiently from acid solutions on a precipitate of zirconium phenylarsonate, and the best pH range for this coprecipitation was investigated (Experimental, J), even strongly acid solutions being suitable.

In the presence of reducing agents (SO_2 or hydroxylamine hydrochloride), it was found that plutonium was not carried down at all by zirconium phenylarsonate. It was therefore concluded that the phenylarsonate of Pu(III) is soluble.

m-Nitrobenzoate. Pu(IV) may be precipitated on zirconium *m*-nitrobenzoate. The effect of pH on the completeness of the precipitation was investigated in the same way as with phenylarsonic acid (Experimental, K). In the presence of reducing agents, plutonium was not carried down on the precipitate of zirconium *m*-nitrobenzoate. It was therefore concluded that the *m*-nitrobenzoate of Pu(III) is soluble.

(d) *Compounds of sexavalent plutonium.* Ammonium plutonate. This salt may be prepared by adding ammonium hydroxide to a hot solution of a plutonium salt which has been oxidised to the sexavalent state with argentic nitrate; it is thereby obtained as a brownish-yellow precipitate which may be filtered off after it has cooled and stood until coagulated. The composition of ammonium plutonate has not been determined.

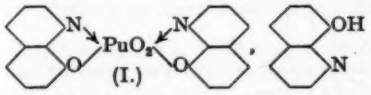
On account of the similarity between the chemistry of uranium and of plutonium in their sexavalent states, the terms " plutonate " and " plutonyl " have been used in the present paper to describe the sexavalent compounds of plutonium.

Plutonyl fluoride. Sexavalent plutonium is not precipitated on a lanthanum fluoride carrier in the presence of an excess of hydrofluoric acid. By this method, plutonium can readily be separated from lanthanum.

Plutonyl nitrate. Ammonium plutonate dissolves readily in nitric acid to give an orange solution, which, by analogy with uranium, is believed to contain plutonyl nitrate, $PuO_2(NO_3)_2$. At low pH values, the solution appears pink, and as the pH is increased, the colour becomes progressively more orange.

Ethyl ether and nitromethane extracted plutonyl nitrate from its aqueous solutions saturated with ammonium nitrate.

Sodium plutonyl acetate. Addition of sodium acetate solutions to a mixed plutonyl and ammonium nitrate solution (prepared by dissolving ammonium plutonate in nitric acid) slowly precipitates crystals similar in appearance to those of sodium uranyl acetate, but pale mauve in colour. The compound is presumably sodium plutonyl acetate.



(I.)

Plutonyl " oxinate." 8-Hydroxyquinoline (" oxine ") precipitates plutonyl ions quantitatively in the pH range 3·5—9. The plutonium content of this *oxinate* was determined as described in Experimental (L). The weight of the complex obtained agreed with the structure (I) for the oxinate, which therefore appears to be the analogue of the corresponding uranyl complex.

IV. *Complex Formation by Plutonium.*—(a) *Inorganic complex ions.* The oxidation–reduction potentials for the Pu(III)–Pu(IV) couple are about + 0·72 volt in 1N-sulphuric acid, + 0·99 volt in 1N-hydrochloric acid, and + 0·86 volt in 1N-perchloric acid. This variation indicates that there must be a tendency towards complex formation with the anion in at least two of the three acids, but the electrochemical evidence does not indicate in which acids this occurs. The presence of a high concentration of chloride ions inhibited the coprecipitation of Pu(III) on a lanthanum fluoride carrier, whereas the sulphate ion showed no real effect. This indicates that Pu(III) ions probably form complexes in chloride solutions. Similarly, ammonium thiocyanate completely inhibited the coprecipitation of Pu(IV) on a carrier of zirconium phenylarsonate or *m*-nitrobenzoate, thus indicating that Pu(IV) ions probably form complexes with the thiocyanate ion.

The presence of alkali carbonates interfered with the extraction of the acetylacetone complex of Pu(IV) into benzene. Experiments with visible quantities of plutonium showed that Pu(IV) salts, including the fluoride, dissolve completely in excess of ammonium carbonate.

Experiments with tracer amounts of plutonium showed that Pu(IV) coprecipitated with lanthanum oxalate could be washed off the lanthanum precipitate with hot or cold ammonium oxalate solution much more readily than could Pu(III). The solubility of Pu(IV) oxalate in ammonium oxalate was confirmed by using visible quantities of plutonium. Pu(IV) fluoride was also found to be readily soluble in ammonium oxalate solution.

(b) *Organic complexes of plutonium.* A brief survey of the behaviour of Pu(III), Pu(IV), and Pu(VI) towards some of the commoner organic complexing reagents was made. The results are contained in Experimental (M). In some cases, the reaction between the plutonium ion and the organic reagent was studied in more detail, using tracer concentrations of plutonium.

Diketone complexes. The extraction coefficient (defined as the ratio of the concentrations

of plutonium in the solvent and the aqueous layer) was measured at various pH's for the systems Pu(IV), water, benzene, and acetylacetone, trifluoroacetylacetone, or benzoylacetone. With the first two diketones, the extraction coefficient rose from 0·5 at pH 1 to an almost constant value of 80 at pH's of greater than 5 for acetylacetone and greater than 4 for trifluoroacetylacetone. The benzoylacetonate gave a maximum extraction coefficient of 8 at a pH of 4. At higher pH's, the extraction coefficient decreased.

Salicylate complex. The extraction coefficient was measured for the system Pu(IV), amyl acetate, salicylic acid, and water at different concentrations of salicylic acid and at two different pH's. The detailed results are given in Experimental (N). In general, the extraction coefficient increased with increasing salicylate concentration in the aqueous layer, but at the higher pH, it was lower for a given salicylate concentration than for the same salicylate concentration at the lower pH. The irregularity of some of the results is believed to be due to the fact that a considerable proportion of the plutonium adhered to the glass walls of the vessels at the pH's used.

Experimental.

General Methods.—(a) *Preparation and purification of plutonium compounds.* During the present work, several methods were used for the initial purification of plutonium and for its recovery from the residues of previous experiments. The most useful method was found to be the one already described by Seaborg *et al.* (*loc. cit.*, p. 367) in which plutonium is precipitated with a carrier of lanthanum fluoride, and then separated from the lanthanum fluoride by making use of the solubility of the fluoride of sexavalent plutonium.

The plutonium in the ter- or quadri-valent state is precipitated on a carrier of lanthanum fluoride by the method described above. The precipitate is then dissolved by fuming with sulphuric or perchloric acid, and the solution is diluted with water. The plutonium is then oxidised to the sexavalent state: potassium permanganate in hot solution was found to be the most convenient oxidising agent for this purpose. The lanthanum is then precipitated by the addition of hydrofluoric acid, leaving the plutonium in solution.

The final purification of the plutonium may be carried out by evaporating the solution to fuming to eliminate the excess of hydrofluoric acid, reducing the plutonium to the tervalent state by warming with an excess of 6% sulphurous acid solution, and then precipitating the plutonium as $Pu(OH)_3$ by the addition of ammonium hydroxide.

The $Pu(OH)_3$ may then be dissolved in sulphuric acid, the plutonium converted to the quadrivalent state by evaporating the solution to dryness in air, and then successively precipitated as peroxide and iodate until the desired degree of purity has been reached.

(b) *Methods of determining plutonium.* Counting of α-particles provides a rapid method for carrying out determinations of relative amounts of plutonium when working with tracer quantities of the element. The half-life of ^{239}Pu is $2·4 \times 10^4$ years (Seaborg, *loc. cit.*). This corresponds to the production of 138×10^6 α-particles/min./mg. Pu.

Plutonium may be weighed as $Pu(SO_4)_2$, PuO_2, or $Pu(IO_3)_4$. The sulphate is particularly convenient, since it may be prepared by fuming many plutonium compounds to dryness with sulphuric acid. The iodate is a useful form in which to weigh small amounts of Pu since it contains only 25·46% of Pu.

It has already been mentioned that permanganate titration of Pu(III) or Pu(IV) may be carried out in hot acid solutions. Titration of the iodine liberated in sulphate solution by the oxidation of iodide ions by Pu(IV) ions is not a convenient method for routine estimation of plutonium because the reaction is rather slow. In chloride solutions, the reaction is faster, but the titration is still not satisfactory.

(A) About 1 mg. of plutonium was purified and precipitated from sulphate solution as its insoluble iodate by addition of a solution of iodic acid. The precipitate was dried at 100° and weighed in a platinum crucible. It was then ignited to constant weight at a dull red heat in air. 3·532 Mg. of iodate gave a plutonium compound weighing 1·021 mg. after ignition. The loss of weight agrees well with the reaction $Pu(IO_3)_4 \longrightarrow PuO_2 + 5O_2 + 2I_2$. The weights of iodate and oxide correspond to a valency of 3·92 for the middle oxidation state of plutonium. The 1·021 mg. of dioxide formed in this experiment was converted into sulphate by fuming to dryness three times with sulphuric acid. The *sulphate* weighed 1·616 mg.; *i.e.*, the sulphate contains 63·2% of PuO_2 [$Pu(SO_4)_2$ requires PuO_2, 62·9%].

(B) (i) During a determination of the oxidation–reduction potential of the Pu(IV)–Pu(IV−n) couple, it was found that a plot of the potential of a platinum electrode against the logarithm of the concentration ratio of Pu(IV) to Pu(IV−n) gave a straight line of slope 0·048 volt at 23°. This corresponds most nearly to the theoretical value of 0·059 volt for a single-electron transfer.

(ii) It was found that in sulphate solutions, the Pu(IV) ion will oxidise the iodide ion to iodine. The iodine which was liberated by 2·206 mg. of $Pu(SO_4)_2$ gave a titre of 0·47 ml. of 0·0103N-sodium thiosulphate. This corresponds to a valency difference of 0·95 between the middle and the lower state of plutonium.

(iii) 0·814 Mg. of $Pu(SO_4)_2$ was titrated in 1N-sulphuric acid solution with approximately 0·005N-potassium permanganate. Reaction was very slow at room temperature, but proceeded rapidly at 60°. After completion of the titration, the plutonium was reduced to the tervalent state by warming with sulphurous acid solution. The excess of sulphur dioxide was driven off by evaporating the solution to a very small volume in a stream of purified carbon dioxide. The tervalent plutonium was then titrated at room temperature to the quadrivalent state with the same permanganate solution. The end-point was quite definite and stable. On warming the solution to 60°, the pink colour of the end-

point faded, and a further quantity of permanganate reacted as the plutonium was oxidised to the highest valency state.

In four such cycles, the average volume of permanganate required to oxidise the Pu(III) to Pu(IV) was 0·37 ml. The volume required to oxidise the Pu(IV) to the highest valency state was almost exactly twice as much, *viz.*, 0·72 ml.

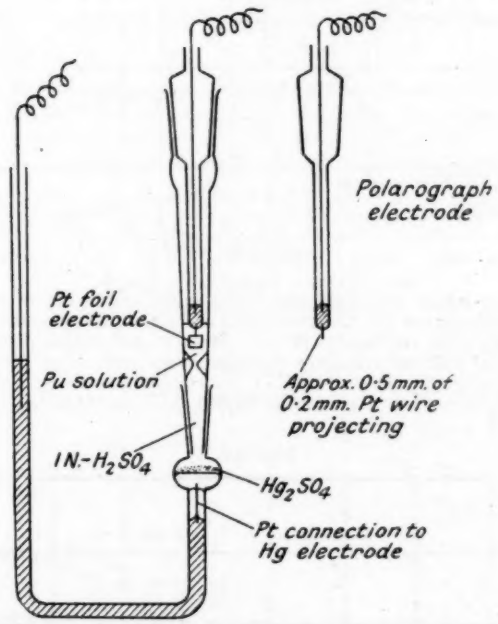
(C) Potentials of the cell

$$Hg|Hg_2SO_4\ (s)\ 1N\text{-}H_2SO_4|1N\text{-}H_2SO_4|1N\text{-}H_2SO_4\ \begin{matrix}Pu(III)\ (c_1)\\ Pu(IV)\ (c_2)\end{matrix}|Pt$$

were measured. The cell is shown in Fig. 1.

The ratio of c_1 to c_2 was varied by mixing in various proportions stock solutions of Pu(IV) sulphate and of Pu(III) sulphate, both in 1N-H_2SO_4. The Pu(III) solution was made as and when required by both electrolytic reduction at a platinum cathode of a Pu(IV) solution.

FIG. 1.



Cell used for polarography and for E_0 *measurements (half actual size).*

The potentials were determined at 23°. They became steady within 5 mins. after insertion of the platinum electrode into the cell. The values are recorded below:

Potentials of the couple Pu(III)–Pu(IV).

Concn. of Pu(III) in solution, M.	Concn. of Pu(IV) in solution, M.	Potential, volt.	Concn. of Pu(III) in solution, M.	Concn. of Pu(IV) in solution, M.	Potential, volt.
0·00404	0·00058	0·0289	0·00152	0·00354	0·0825
0·00354	0·00118	0·0420	0·00101	0·00412	0·0931
0·00304	0·00177	0·0548	0·00051	0·00471	0·1050
0·00227	0·00265	0·0581			

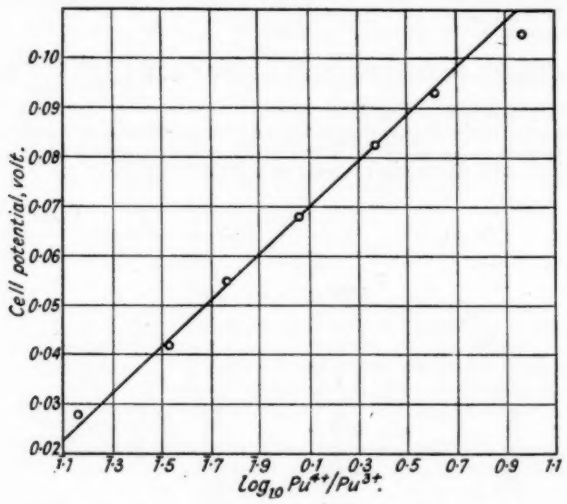
The molar concentrations were estimated by diluting a small volume of each of the stock solutions, and α-counting aliquots of the dilute solutions. There may thus be errors of up to 15% in the absolute concentration values, but as the same counter and counting technique were used for both of the solutions, the relative concentrations are believed to be correct to ± 5%.

Fig. 2 shows the linear variation of the potential with $\log_{10} c_2/c_1$. The potential when $c_2 = c_1$ was + 0·064 volt, with the platinum electrode positive. Assuming that the potential of the mercurous sulphate electrode is + 0·66 volt on the hydrogen scale, this gives a value of + 0·72 volt for the couple with equal concentrations. The molal standard potential is therefore in the region of + 0·72 volt.

Similar experiments designed to measure the potential of the same couple in 1N-hydrochloric acid and 1N-perchloric acid failed, because in several trials with different lots of plutonium the potentials drifted badly. However, the observed values of the equimolar potentials were always close to the potentials of the polarographic waves in the same solutions (see p. 1018).

(D) Polarographic experiments were carried out in 1N-sulphuric, -perchloric, and -hydrochloric acids (see Figs. 3, *a*, *b*, and *c*).

FIG. 2.



A small platinum wire micro-electrode replaced the foil electrode of the cell in Fig. 1, and a sintered-glass plug was substituted for the constriction. A dropping-mercury electrode could not be used because mercury dissolves anodically in the range of potentials studied. For polarograms in hydrochloric acid, a normal calomel reference electrode was used. For perchloric acid solutions, the reference electrode was $Hg|Hg_2Cl_2$ (s) + 0·1N-HCl + 1N-$HClO_4$| with a bridge solution of 1N-$HClO_4$. In sulphuric acid, the reference electrode was $Hg|Hg_2SO_4$ (s) + 1N-H_2SO_4|.

FIG. 3 (*a*).

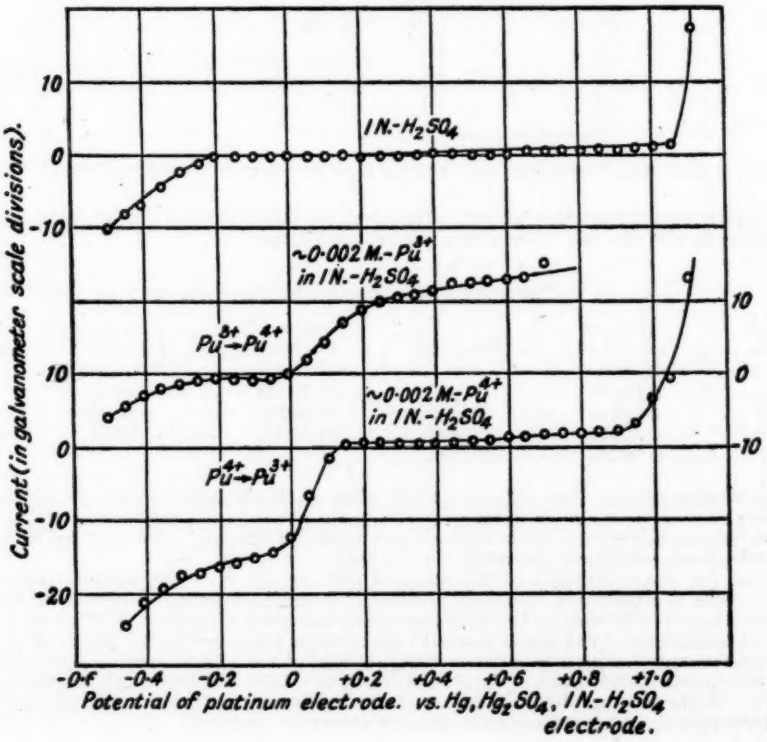


FIG. 3 (*b*).

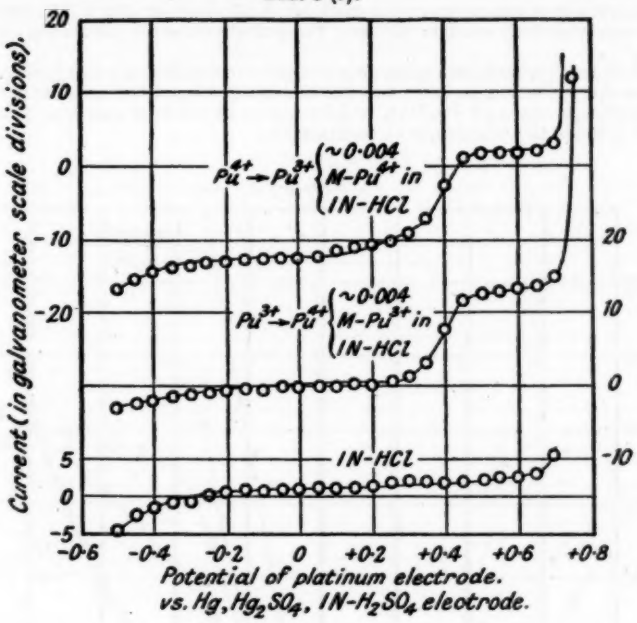
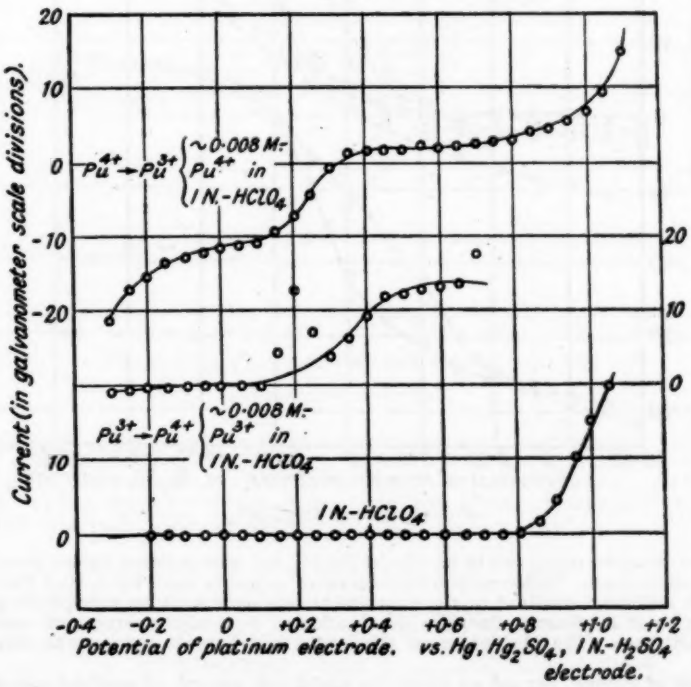

Current (in galvanometer scale divisions).
$Pu^{4+} \rightarrow Pu^{3+}$ ~0·004 M-Pu^{4+} in 1N-HCl
$Pu^{3+} \rightarrow Pu^{4+}$ ~0·004 M-Pu^{3+} in 1N-HCl
1N-HCl
Potential of platinum electrode.
vs. Hg, Hg_2SO_4, 1N-H_2SO_4 electrode.

FIG. 3 (*c*).


Current (in galvanometer scale divisions).
$Pu^{4+} \rightarrow Pu^{3+}$ ~0·008 M-Pu^{4+} in 1N.-$HClO_4$
$Pu^{3+} \rightarrow Pu^{4+}$ ~0·008 M-Pu^{3+} in 1N.-$HClO_4$
1N.-$HClO_4$
Potential of platinum electrode. vs. Hg, Hg_2SO_4, 1N.-H_2SO_4 electrode.

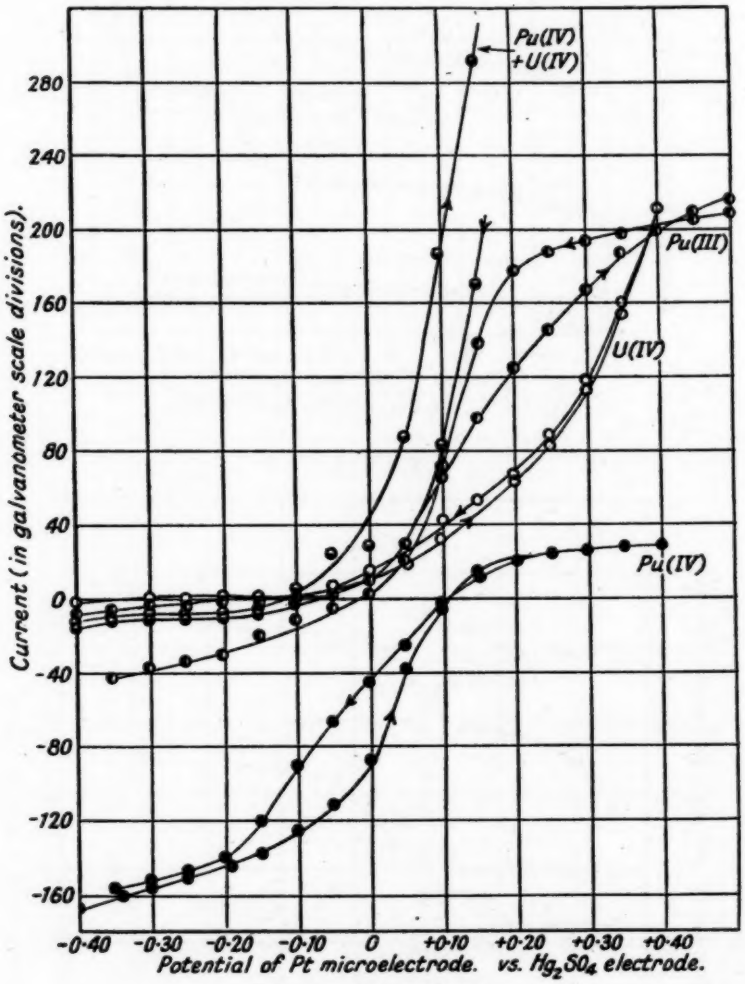
The polarograms in perchloric acid solution were carried out at 23°. In all other cases, the cell was held at 30° in a vibration-free thermostat.

(E) Small volumes of concentrated uranous sulphate and uranous chloride in their respective 1N-acids were added to solutions of Pu(IV) in 1N-sulphuric and hydrochloric acids. In both cases the Pu(IV) reduction wave disappeared within 2 or 3 minutes of the addition and was replaced by a wave starting

in the same place as the Pu(III) wave in the same solution (Figs. 4 and 5). The concentrations of Pu(IV) in these experiments were chosen so that after addition of the U(IV) solution, the Pu concentrations were equal to those used in plotting the polarograms for pure Pu(III) solutions given in the same diagram.

U(IV) in sulphuric and hydrochloric acids does not give an oxidation wave in this range of potentials. The great height of the oxidation wave in the Pu–U mixtures must be due to the oxidation of U(IV) at the electrodes in the presence of Pu(III), which acts as an electron carrier. (The uranium concentration was about 5 times the plutonium concentration.)

FIG. 4.



Polarograms in 1N-H_2SO_4.

(F) Experiments were carried out in which the Pu(IV) ion was oxidised by the perdisulphate ion in the presence of silver ions. Different concentrations of reagents were tried, and the fraction of the plutonium which had been oxidised in the experiment was estimated by precipitating the remaining Pu(IV) on a carrier of lanthanum fluoride (the fluoride of sexavalent plutonium remains in solution under these conditions). The plutonium on the lanthanum fluoride carrier was then estimated by α-counting.

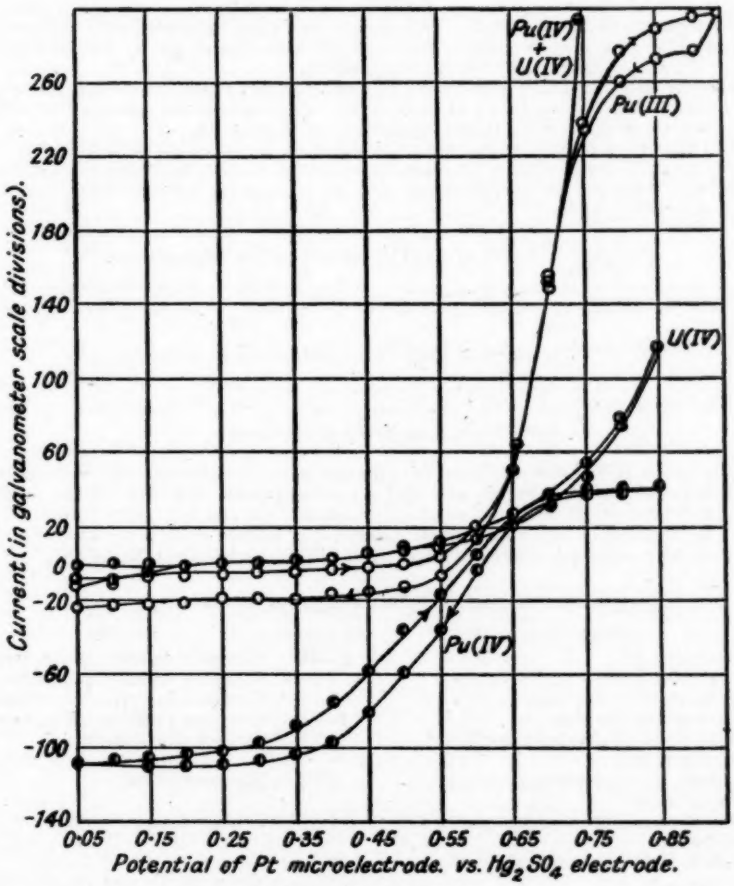
Concentrations of 0·2 mg. per ml. of silver ion and 2 mg. per ml. of perdisulphate ion were found to be sufficient. Oxidation of the plutonium took place when the solutions were heated to 80° and then allowed to cool and stand for 20 minutes. The presence of nitrate ions (about 0·5M) appeared to be advantageous. Perchloric acid up to 2M was without influence of the reaction.

(G) (i) A sample of plutonium peroxide precipitated from sulphate solution was washed free from excess of hydrogen peroxide, suspended in 1N-sulphuric acid, and titrated with potassium permanganate. It was found that on warming the solution very slightly, a reaction took place and the per-

oxide went into solution. After 0·71 ml. of permanganate had been used, the peroxide appeared to have dissolved completely, and further permanganate only reacted at a somewhat higher temperature. The volume of permanganate required at this higher temperature was 0·47 ml.

The second half of this titration was believed to represent the oxidation of Pu(IV) to Pu(VI). This was confirmed by reducing the plutonium to Pu(III) with sulphur dioxide, and evaporating the solution to fuming in air to remove the excess sulphur dioxide and convert the Pu(III) into Pu(IV). The same volume (0·47 ml.) of permanganate was used when the Pu(IV) obtained in this way was titrated to Pu(VI).

FIG. 5.



Polarograms in 1N-HCl.

(ii) A second sample of the peroxide, precipitated from sulphuric acid solution, washed three times with water, and dried to constant weight over silica gel at room temperature, was dissolved in concentrated nitric acid. The sulphate ion present in the solution was determined by precipitating it as barium sulphate. The plutonium was then precipitated from the solution as hydroxide and weighed as PuO_2. The following results were obtained:

Wt. of peroxide, mg.	2·255
Wt. SO_4, mg.	0·216
Wt. Pu, mg.	1·704
Total, mg.	1·920
Remainder, mg.	0·335

(H) A small weight of lanthanum nitrate in aqueous solution was added to a dilute perchloric acid solution containing a tracer quantity of quadrivalent plutonium; 48% hydrofluoric acid was then added until its concentration in the Pu–La solution was 12%. The precipitate of lanthanum fluoride was allowed to settle, and a further quantity of lanthanum nitrate, equal to the first amount, was then slowly added with good stirring.

After standing for about 30 minutes with occasional stirring, the solution was centrifuged to separate the fluoride precipitate. The supernatant solution was removed, and the precipitate washed several times with dilute hydrofluoric acid. The lanthanum fluoride was then spread on a sample tray, and the plutonium estimated by α-counting. The results are given below:

Precipitation of Pu(IV) *on lanthanum fluoride.*

Total wt. of La used, mg./ml. of Pu soln.	0·35	0·093	0·034	0·017
% Pu remaining in solution	1·49	1·94	6·11	10·4

(I) A sample of sulphate crystals (see p. 1012) was separated from the solution, washed with acetone, dried at room temperature and weighed. The sample was then converted into the anhydrous salt by fuming to dryness with sulphuric acid. The crystals were found to be the *tetrahydrate* [Found: $Pu(SO_4)_2$, 85·8. $Pu(SO_4)_2.4H_2O$ requires $Pu(SO_4)_2$, 85·6%].

(J) Experiments were carried out to discover over what pH range zirconium phenylarsonate could be used as a carrier for tracer quantities of plutonium. Zirconyl nitrate solutions were added to dilute perchloric acid solutions containing tracer quantities of plutonium. The pH's of the solutions were then adjusted to various values by the addition of either more perchloric acid or ammonia. An excess of saturated aqueous phenylarsonic acid solution was then added, and the precipitate of zirconium phenylarsonate was removed by centrifuging, and its plutonium content estimated by α-counting. The results are shown herewith.

The precipitation of Pu(IV) *on zirconium phenylarsonate.*

pH	0·1	0·19	0·33	1·45	1·90	3·95
% Pu precipitated by 0·2mg./ml. of Zr	87·6	88·5	93·9	93·7	90·0	93·2

(K) *Precipitation of* Pu(IV) *on zirconium* m-*nitrobenzoate.*

pH	0·39	1·46	1·88	3·80
% Pu precipitated by 0·2 mg./ml. of Zr	5·1 *	91·0	95·4	93·3

* Zr not completely precipitated.

(L) 9·457 Mg. of $Pu(SO_4)_2$ were dissolved in sulphuric acid and oxidised by heating for several hours at 90° on a steam-bath with an excess of sodium perdisulphate. The pH of the solution was then adjusted to about 5, and about 5 equivs. of oxine dissolved in acetic acid were added. The precipitate was coagulated by heating on the steam-bath, filtered off, washed with hot water, dried at 130°, and weighed. The *oxinate* weighed 15·713 mg. [Found: Pu, 33·4. $PuO_2(C_9H_6ON)_2.C_9H_7OH$ requires Pu, 33·9%].

(M) *Reaction of plutonium with organic complexing reagents.*

Ion.	Reagent.	pH range.	Reaction.
Pu(IV)	Acetylacetone	2—10	Complex extractable in benzene
Pu(IV)	Benzoylacetone	3	Complex extractable in benzene
Pu(IV)	Monofluoroacetylacetone	3	Complex extractable in benzene
Pu(IV)	Trifluoroacetylacetone	2—4	Complex extractable in benzene
Pu(IV)	*p*-Dimethylaminobenzeneazophenylarsonic acid	4	Orange precipitate
Pu(III)	*p*-Dimethylaminobenzeneazophenylarsonic acid	4	No precipitate
Pu(IV)	*p*-Dimethylaminobenzeneazophenylarsinic acid	4	Orange-red precipitate
Pu(III)	*p*-Dimethylaminobenzeneazophenylarsinic acid	4	No precipitate
Pu(IV)	3-Nitro-4-hydroxyphenylarsonic acid	2·5	Pale greenish-buff precipitate, Pu carried down on Zr salt
Pu(III)	3-Nitro-4-hydroxyphenylarsonic acid	2·5	No ppt. Pu not carried down on Zr salt
Pu(IV)	*m*-Nitrophenylarsonic acid	2·5	Pale greenish-buff ppt. Pu carried down on Zr salt
Pu(III)	*m*-Nitrophenylarsonic acid	2·5	No ppt. Pu not carried down on Zr salt
Pu(IV)	Phenylarsonic acid	2	Pale greenish-buff ppt. Pu carried down on Zr salt
Pu(III)	Phenylarsonic acid	2	No ppt. Pu not carried down on Zr salt
Pu(IV)	*n*-Propylarsonic acid	2	Pale greenish-buff ppt. Pu carried down on Zr salt
Pu(III)	*n*-Propylarsonic acid	2	No ppt. Pu not carried down on Zr salt
Pu(IV)	*m*-Nitrobenzoic acid	1·5	Pale greenish-buff ppt. Pu carried down on Zr salt
Pu(III)	*m*-Nitrobenzoic acid	1·5	No ppt. Pu not carried down on Zr salt
Pu(IV)	Sebacic acid	1—2	Pu carried down on Zr salt
Pu(III)	Sebacic acid	1—2	Pu poorly carried down on Zr salt
Pu(IV)	5-*p*-Acetamidophenylazo-8-hydroxyquinoline	4	Complex extractable in amyl acetate. Insol. in water
Pu(IV)	8-Hydroxyquinoline	—8	Purple-brown ppt. extractable in amyl acetate

Ion.	Reagent.	pH range.	Reaction.
Pu(VI)	8-Hydroxyquinoline	4—8	Orange-brown ppt. extractable in amyl acetate
Pu(IV)	1′-Sulphonaphthalene-4′-azo-5 : 8-dihydroxyquinoline	3	Purple ppt.
Pu(IV)	Anthranilic acid	3	Complex extractable in amyl acetate
Pu(IV)	Cinnamic acid	2·5—4·5	Complex extractable in amyl alcohol
Pu(IV)	Cresotinic acid	2·5—4·5	Complex extractable in amyl acetate
Pu(IV)	2 : 4-Dihydroxybenzoic acid	3	Complex extractable in methyl *iso*butyl ketone
Pu(IV)	2 : 4-Dinitrosalicylic acid	3	Complex extractable in amyl acetate
Pu(IV)	Salicylic acid	2—3	Complex extractable in amyl acetate. Pu carried down on Th, La and Zr salts
Pu(IV)	Benzoic acid	2	Green-yellow ppt.
Pu(IV)	Citric acid	1—11	Soluble complex
Pu(IV)	Dihydroxytartaric acid	1	Pu carried down on Th salt
Pu(III)	Dihydroxytartaric acid	1	Pu poorly carried on Th salt
Pu(IV)	3 : 5-Dinitrobenzoic acid	3	Complex extractable in amyl acetate
Pu(IV)	Phthalic acid	2	Pu carried down on Zr salt
Pu(III)	Phthalic acid	2	Pu not carried down on Zr salt
Pu(IV)	Tartaric acid	1—11	Soluble complex
Pu(VI)	Tartaric acid	1—11	Soluble complex
Pu(IV)	Thiobarbituric acid	2	Pu carried down on Th, Zr, and La salts
Pu(III)	Thiobarbituric acid	3	Pu poorly carried down on Th, Zr, and La salts
Pu(IV)	" Cupferron "	0·5—2	Complex extractable in chloroform
Pu(IV)	Ethylenediamine	—	Brown ppt., insol. in water and organic liquids
Pu(IV)	α-Nitroso-β-naphthol	2	Complex extractable in methyl *iso*butyl ketone
Pu(IV)	Sodium benzenesulphinate	2	Buff ppt. not extractable in amyl acetate
Pu(VI)	Sodium benzenesulphinate	2	Complex extractable in amyl acetate
Pu(VI)	Sodium diethyldithiocarbamate	3	Purple-brown complex extractable in amyl acetate or amyl alcohol

(N) *Extraction of* Pu(IV) *salicylate into amyl acetate.*

Salicylate concn. in aq. layer, moles/l.	pH of aq. layer.	Extrn. coeff. of Pu.	Salicylate concn. in aq. layer, moles/l.	pH of aq. layer.	Extrn. coeff. of Pu.
0·0058	4·0	0·23	0·053	5·2	0·15
0·0116	4·0	0·16	0·214	5·2	0·22
0·0232	4·0	0·64	0·428	5·2	3·7
0·0464	4·0	7·9	0·642	5·2	4·8
0·0696	4·0	3·4	0·856	5·2	2·1
0·0928	4·0	4·7	1·07	5·2	12·8
0·116	4·0	8·12			

This work was carried out for the National Research Council of Canada, Atomic Energy Division, at Montreal, Que., and Chalk River, Ont. Two of the authors (B. G. H. and A. G. M.) were on leave from Messrs. Imperial Chemical Industries, Ltd. The authors are indebted to Mr. A. J. Cruikshank for help with some sections of the work

CHALK RIVER, ONTARIO. [*Received, March 6th,* 1947.]

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189. *Production of Antibiotics by Fungi. Part III. Javanicin. An Antibacterial Pigment from* Fusarium javanicum.

By H. R. V. ARNSTEIN and A. H. COOK.

The isolation and characterisation of *javanicin* is described. It is regarded as a 5 : 8-dihydroxy-6-acetonyl-1 : 4-naphthaquinone carrying additional β-methyl and β-methoxyl groupings.

IT was observed (Arnstein, Cook, and Lacey, *Nature*, 1946, **157**, 333; see also Part I, Cook and Lacey, *Brit. J. Exp. Path.*, 1945, **26**, 404) that certain metabolism solutions obtained from *Fusarium javanicum* inhibited the growth of *Staphyllococcus aureus* at a dilution of 1 : 100 and were also very active against the acid-fast *Mycobacterium phlei*. In view of the possibility of the active principle or principles having a useful inhibitory action against *M. tuberculosis* their nature

was studied more closely. Their production under various conditions and some biological properties are described elsewhere (Part II, Arnstein, Cook, and Lacey, *Brit. J. Exp. Path.*, 1946, **27**, 349) and the present communication records experiments on their chemical nature.

The materials of the present study were only produced under selected conditions; the most notable requirement was the presence of " Bactotryptone " in addition to mineral salts and glucose in the fermenting solution. Bactotryptone could be replaced by some but not all similar preparations, though the characteristic essential for the production of antibacterial activity could not be distinguished. Under the selected conditions the active solutions were heavily pigmented, resembling red ink in colour. The activity could be completely removed from slightly acid solutions by extraction with solvents such as ether, and the crude recovered pigment accounted for the whole of the activity of the original solutions. After preliminary experiments had shown that the antibacterial activity was insensitive to heat, acid, alkali, and solvents, attempts were made to purify the active principles, for example, by the ordinary methods of chromatography but without success. It was found that the active principle could be removed from the crude ethereal extract by shaking with sodium carbonate but not by sodium hydrogen carbonate, and that it could be returned from aqueous sodium carbonate to ether by neutralising the solution. The final solution was still strongly coloured (red-orange) and, as inactive pigment fractions were rejected at each point, it was apparent that several probably chemically similar pigments were initially present. The active solution on concentration gave a pigment which could be crystallised. The behaviour of the crystalline material varied from batch to batch. One compound, m. p. 207·5—208° (decomp.), was invariably obtained and sometimes another compound, m. p. 213—214° (decomp.), formed a second component. Occasionally a product, m. p. 178—179°, was obtained which was analytically intermediate between the two compounds, and as the m. p. behaviour was reproduced by an equimolecular mixture of the two it seems not unlikely that the third product was a molecular compound of the other two. Both compounds were very active antibacterial agents (see Arnstein, Cook, and Lacey, *loc. cit.*) and there was no reason to doubt that the whole of the activity of the original solutions was due to these two crystalline pigments. They were very similar in character but detailed attention could be given only to the compound, m. p. 207·5—208°, which, as it does not appear to have been isolated previously, is conveniently termed *javanicin*; the compound, m. p. 213—214°, contained one oxygen atom more than javanicin and is therefore termed *oxyjavanicin*.

The pigments produced by *Fusaria* are known to be very variable and delicately dependent on the conditions of growth (Brown and Horne, *Ann. Bot.*, 1924, **38**, 379; Brown, *ibid.*, 1925, **39**, 373; Sideris, *J. Agric. Res.*, 1925, **30**, 1011); probably for this reason there have been few occasions when *Fusarium* pigments have been isolated in pure condition and studied chemically. Ashley, Hobbs, and Raistrick (*Biochem. J.*, 1937, **31**, 388) isolated two pigments, rubrofusarin and aurofusarin, from *F. culmorum*. Aurofusarin is so different from the present pigments that it can hardly be confused with them, whilst the distinctive nature of rubrofusarin is made clear below. Javanicin and oxyjavanicin differ from the earlier pigments in diffusing into and being isolated from the medium instead of from the mycelium; the mycelium of *F. javanicum* although coloured did not yield any remarkable quantity of antibacterial pigment. Solid media on which *F. javanicum* was grown also became deeply pigmented; on the other hand, those on which *F. culmorum* was grown were scarcely coloured although the mycelia were very bright (Brown and Horne, *loc. cit.*). Mull and Nord (*Arch. Biochem.*, 1944, **4**, 422) mention diffusing *Fusaria* pigments and the experiments of Sideris (*loc. cit.*) particularly clearly demonstrate their formation, so the production of javanicin and oxyjavanicin is possibly not restricted to *F. javanicum*, and other species may produce nearly related pigments.

Javanicin contained only carbon, hydrogen, and oxygen. It apparently contained no easily hydrolysed groupings and could be heated in an autoclave without significant loss of activity, though very dilute solutions on prolonged exposure to light lost both colour and antibacterial activity, presumably as a result of photochemical oxidation.

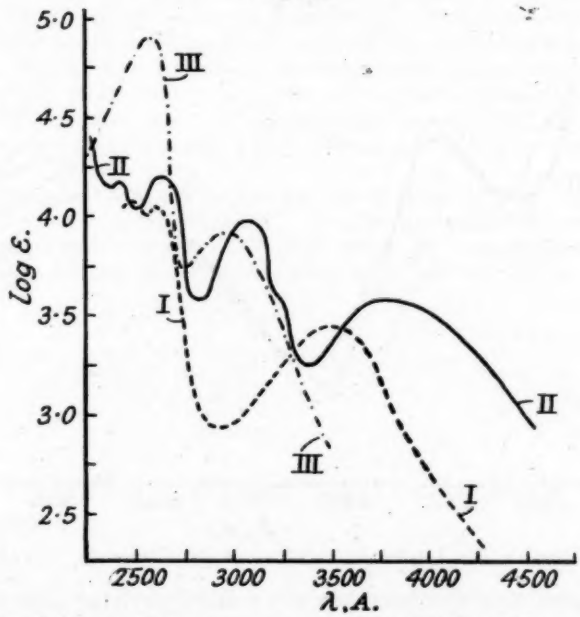
Analyses and determinations of molecular weight on different samples of javanicin from several batches indicated the formula $C_{18}H_{14}O_6$. Of the six oxygen atoms one was present as a methoxyl group. The molecule contained three active hydrogen atoms, but on acetylation in presence of concentrated sulphuric acid it yielded a yellow compound of the empirical and molecular formula, $C_{17}H_{14}O_6$, *i.e.*, a monoacetyl derivative of a hitherto unknown anhydrojavanicin. This *monoacetylanhydrojavanicin* contained one methoxyl group.

The reality of the dehydration of javanicin during acetylation was confirmed by the behaviour of the pigment itself. Javanicin showed signs of undergoing dehydration in sulphric acid solution and under other conditions, but reaction was most satisfactory with ethereal hydrogen

chloride containing zinc chloride. Under these conditions javanicin smoothly lost 1 mol. of water to give *anhydrojavanicin*, $C_{15}H_{12}O_5$, which on acetylation passed into the acetyl compound previously obtained directly. Anhydrojavanicin was chemically and physically quite distinct from the parent pigment, and contained only one active hydrogen atom in agreement with structure (III) (R = H) developed below. Two more oxygen atoms were revealed as a quinone grouping, for on reductive acetylation anhydrojavanicin was converted into a *leucoanhydrotriacetate*, $C_{21}H_{20}O_8$.

Javanicin anhydromonoacetate and leucoanhydrotriacetate showed spectra which indicated them to be α-naphthaquinone and naphthalene derivatives respectively (Fig. 1). It is known that if the hydroxyl groups of a hydroxynaphthaquinone be acylated, the spectrum loses any features peculiar to the tautomeric hydroxynaphthaquinone structure and reverts to that of a simple naphthaquinone (Macbeth, Price, and Winzor, *J.*, 1935, 325). Incidentally, consideration of the spectra of javanicin and its derivatives excluded the possibility of their being benzoquinone or anthraquinone derivatives; it was moreover impossible to accommodate a summation of other facts noted below on these formulations. Rubrofusarin, $C_{15}H_{12}O_5$, a pigment from

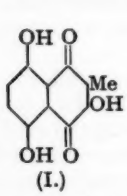
FIG. 1.



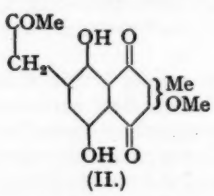
I. *Hydroxydroserone triacetate.* II. *Javanicin anhydromonoacetate.*
III. *Javanicin leucoanhydrotriacetate.*

F. culmorum (Ashley, Hobbs, and Raistrick, *loc. cit.*) appears formally closely related to javanicin, but rubofusarin behaves quite differently especially towards alkalis, with which it gives only a yellow colour, gives derivatives which are clearly distinct from those of javanicin, and is also spectrally quite distinct from javanicin (cf. Mull and Nord, *loc. cit.*). Javanicin gave a deep violet solution with 10% sodium hydroxide, purple solutions with concentrated ammonia or 2N-sodium carbonate, but no colour with sodium hydrogen carbonate. It was decolorised by bromine water or aqueous sodium hydrogen sulphite. The formulation of javanicin as a naphthaquinone derivative was supported by its colour reaction with lead acetate in methanol. Javanicin gave a violet solution; methylnaphthazarin also gave a violet solution, whilst hydroxydroserone (see below) gave a violet precipitate, and Kuhn and Wallenfels (*Ber.*, 1939, **72**, 1411) record that 5 : 8-dihydroxy- and 2 : 5 : 8-trihydroxy-naphthaquinone, echinochrome A, and its trimethyl ether all give violet solutions or precipitates. The formation of a coloured solution rather than a precipitate indicated the absence of any β-hydroxyl group (cf. Kuhn and Wallenfels, *loc. cit.*; see also below). Reaction of javanicin with diazomethane was complex, presumably because of reaction with the side chain, but anhydrojavanicin failed to react under normal conditions. As anhydrojavanicin is regarded as having the angular structure (III), and as only β-hydroxyl

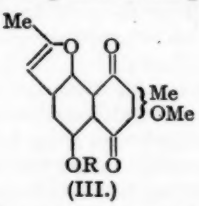
groups in naphthaquinones are methylated under the normal conditions by diazomethane (Kuhn and Wallenfels, *loc. cit.*), this behaviour provides further though indirect evidence of the methoxyl group occupying a β-position. Comparison of the absorption spectrum of javanicin with that of representative hydroxynaphthaquinones revealed that its spectrum was practically



(I.)



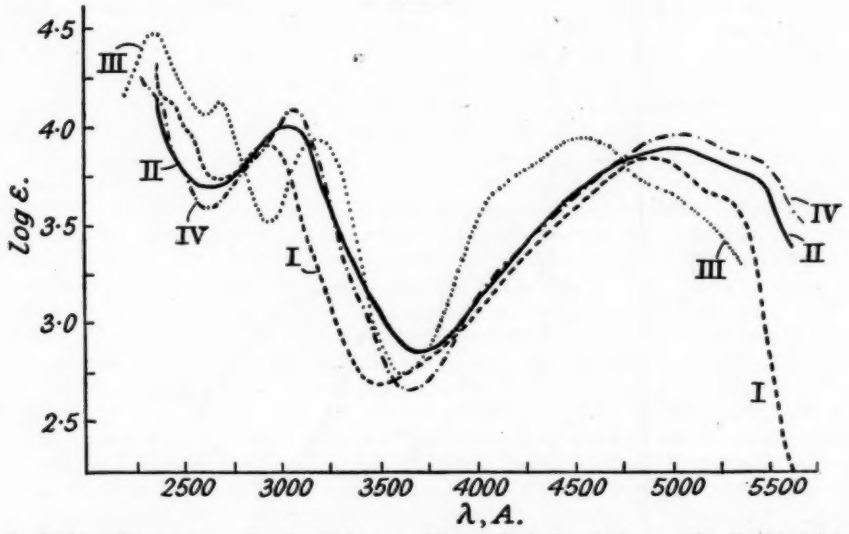
(II.)



(III.)

coincident with that of hydroxydroserone (Macbeth, Price, and Winzor, *loc. cit.*) (Fig. 2) (3 : 5 : 8-trihydroxy-2-methyl-1 : 4-naphthaquinone, I) and the sequel shows that javanicin is indeed closely related structurally to hydroxydroserone, which also gives a magnificent violet colour with alkali (Rennie, *J.*, 1887, **51**, 374).

FIG. 2.



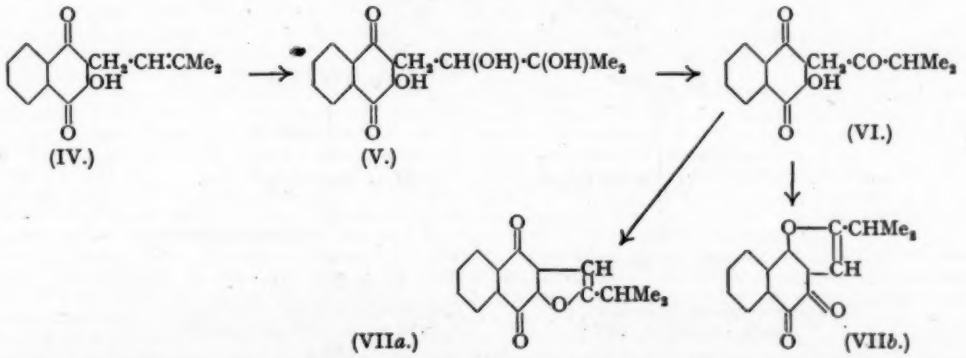
I. *Hydroxydroserone.* II. *Javanicin.* III. *Anhydrojavanicin.* IV. *Oxyjavanicin.*

These facts suggested then that javanicin was a dihydroxylated naphthaquinone carrying in addition to a β-methoxyl group a substituent which was able to undergo dehydration (cyclisation) by interaction with a neighbouring hydroxyl group. In view of the magnificent colour of javanicin in alkali and its acidity, the hydroxyls were believed to be in the *peri*-positions. Attempts were made to confirm this analytically by the formation of a boric acid complex (Macbeth and Winzor, *J.*, 1935, 334) but under conditions which precluded anhydride formation a stable complex proved unobtainable. That two hydroxyls were indeed present was shown by the behaviour of javanicin towards acylating agents under milder conditions than were used in the original experiments described above. When it was acetylated with acetic anhydride in pyridine *diacetyljavanicin*, $C_{19}H_{18}O_8$, was formed, and treatment with benzoyl chloride in pyridine afforded *dibenzoyljavanicin*, $C_{29}H_{22}O_8$. The acylation of a number of hydroxylated naphthaquinones has been described in the literature and no difficulty seems to have been encountered in fully acylating these compounds, so it was concluded that javanicin contained no more than two hydroxyl groups together with a β-methoxyl group.

On oxidation by the Kuhn–Roth method, javanicin gave two molecules of volatile fatty acid indicating two substituents, so the structure could be written in the form $C_{10}HO_2(OH)_2(OMe)RR'$, where $R + R' = C_4H_8O$. For the following reasons the four carbon atoms could only be distributed so that R contained C_1 and R′ contained C_3. The oxygen atom in the grouping C_4H_8O could not be placed on a terminal carbon atom for the side chain could not then have afforded a molecule of volatile fatty acid. If therefore there had been a

C_2,C_3 distribution the substituents would have been Et and COMe [or possibly CH(OH)Me], but these would not reasonably permit cyclisation. The remaining possibilities therefore for R, R′ are Me and CH_2·COMe, or less likely, in view of the analytical results, Me and CH_2·CH(OH)Me. When javanicin was oxidised with sodium hypoiodite or hypobromite, considerable yields of iodoform or bromoform were obtained. Moreover, when javanicin was treated with 2 : 4-dinitrophenylhydrazine a *mono*-2 : 4-*dinitrophenylhydrazone* was formed. Under the same conditions hydroxydroserone failed to react with dinitrophenylhydrazine and it was concluded that javanicin contained the substituents Me and CH_2·COMe. This conclusion was in agreement with the finding that javanicin had no observable optical activity, and that hydrogenation afforded no evidence of an ethylenic linkage. Catalytic hydrogenation resulted in rapid uptake of 1 mol. of hydrogen with disappearance of the colour, which was quickly regenerated in presence of air. From the recovered coloured solution the original pigment could be isolated, and obviously hydrogenation to this extent resulted only in formation of a leuco-compound. A second mol. of hydrogen was slowly absorbed, and further hydrogenation was very slow indeed; this stage corresponds supposedly to reduction of the ketone grouping followed by progressive reduction of the naphthalene nucleus, but no pure hydrocompounds were isolated. This suggested the partial structures (II) and (III) (R = COMe) for javanicin and its anhydromonoacetate respectively. These structures leave one unsubstituted position in the naphthalene nucleus; accordingly, after anhydrojavanicin was treated with bromine under very mild conditions a *monobromoanhydrojavanicin* was isolated. Furthermore, rather prolonged treatment of javanicin or anhydromonoacetyljavanicin with acetic anhydride gave an *acetoxy*-derivative of anhydroacetyljavanicin, $C_{19}H_{16}O_7$. Highly substituted naphthaquinones are known to undergo Thiele–Winter acetylation by this treatment, though with some difficulty.

The ready cyclodehydration of javanicin and its derivatives as pictured above is perhaps paralleled by the behaviour of lapachol (IV). Dihydroxylapachol (V) on dehydration gives, among other products, hydroxy*iso*lapachol (VI), which on further dehydration affords two products formulated by Hooker (*J.*, 1896, **69**, 1360) as (VII*a*) and (VII*b*).

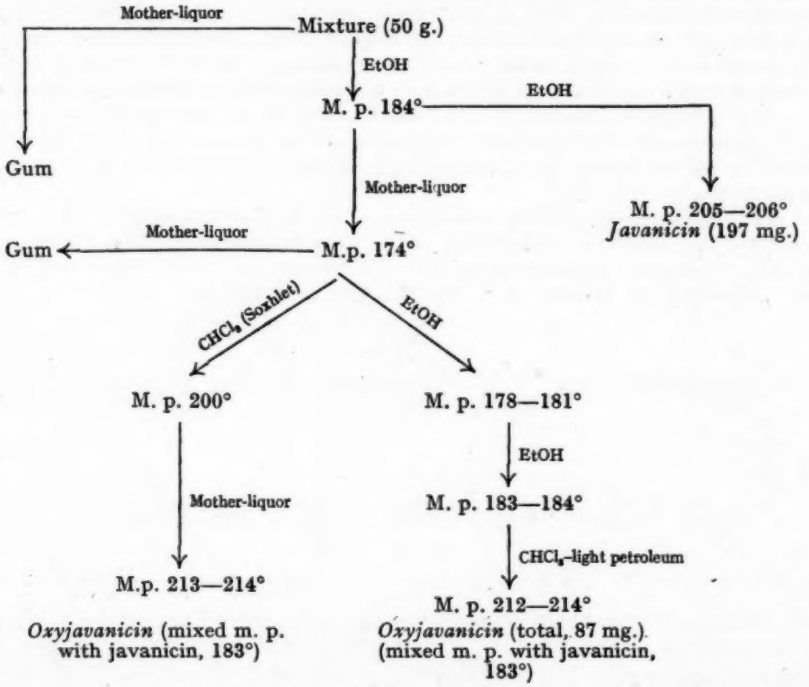


It may be pointed out that quinones of various kinds have been frequently observed to have strong antibacterial actions, and that the action of javanicin (and oxyjavanicin) is undoubtedly due in large measure to the quinone nature. Like that of other quinones, for example, its action is inhibited, though with some difficulty, by compounds containing thiol groupings. On the other hand, it seems equally certain that specific structural effects are exerted. Thus, comparison of javanicin with the nearly related hydroxydroserone showed that the activity of the latter especially towards *Myco. phlei* was surprisingly small (Arnstein, Cook, and Lacey, *Brit. J. Exp. Path.*, 1946, **27**, 349).

Experimental.

Production of Javanicin and Oxyjavanicin.—Stock slope cultures of *F. javanicum* were grown on a medium containing Kepler's malt extract (3%) and agar (2%) in 6″ × 1″ test-tubes. The mycelium of a single slope was pulped with sterile water (50 c.c.), and the suspension (2—3 c.c.) used to inoculate bottles of liquid medium. This technique was adopted to ensure even and prompt growth. The liquid medium contained: Sodium nitrate, 20 g.; potassium chloride, 5 g.; anhydrous magnesium sulphate, 2·5 g.; dipotassium hydrogen phosphate, 10 g.; ferrous sulphate heptahydrate, 0·1 g.; glucose, 400 g.; "Bactotryptone" (Difco) or "Eupepton" (No. 2) (Allen and Hanbury, Ltd.), 50 g.; distilled water to 10 l. The inorganic salts were dissolved separately in small portions of hot distilled water and added to distilled water (*ca.* 8 l.). Glucose in water (1 l.) and bactotryptone or eupepton in water (500 c.c.) were

added, and the volume made up. The medium, which was at pH 6·8—7·0 without further adjustment was distributed into quart-size milk bottles, each containing 400 c.c., furnished with cotton-wool plugs and sterilised at 15 lb. for 15 minutes. The inoculated bottles were incubated, stacked in an almost horizontal position at 25—28° for 10—14 days. The mycelium covered the surface only sparsely; it was highly pigmented (red) from the beginning and the medium became distinctly red after about 7 days. The antibiotic activity and colour of the medium increased to a maximum after about 10 days, the medium then having pH 3. All bio-assays were carried out by the serial dilution method, as plate assays were unreliable, especially on partly purified material. Before assay the solutions were adjusted to pH 7 and sterilised by heat; Seitz filtration resulted in the pigment and antibacterial principles being retained on the filter. (*a*) In a typical batch the filtered metabolism solution (11 l.), which inhibited the growth of *Staph. aureus* at a dilution of 1 : 100, was extracted twice with ether (2·5 l.) previously freed from peroxides. The ethereal solution was twice extracted with saturated aqueous sodium hydrogen carbonate, which removed a mixture of apparently at least several antibacterially inactive pigment components. The remaining ethereal solution was extracted with N-sodium carbonate (4 × 500 c.c.), which removed all the activity. By adjusting the aqueous solution to pH 7 and again extracting with ether (2 l.), the activity and pigment were returned to the organic solvent. The dried ethereal solution was evaporated to 50 c.c., whereupon most of the pigment separated; the mother-liquor yielded only a small quantity of gummy solid, which was rejected. The solid pigment (0·509 g.) had m. p. *ca.* 168° and inhibited the growth of *Staph. aureus* at a dilution of 1 : 200,000. The mixture was crystallised according to the following scheme:



(*b*) In another batch of metabolism medium (20 l.) the mycelium was filtered off, yielding 31 g. of dry material after drying at 100° for several hours. The finely powdered mycelium (20 g.) was extracted (Soxhlet) with light petroleum for 6 hours, no more red pigment then appearing to be extracted. On concentration to small volume (50 c.c.) and cooling, a small quantity of red solid (20 mg.), m. p. 200°, was obtained. One recrystallisation from hot acetone–ethanol (1 : 1) (5 c.c.) afforded pure crystalline material (laths), m. p. 207° (decomp.) alone or mixed with javanicin obtained from the filtrate (see below). (*c*) The filtrate from (*b*) (20 l.) was extracted with ether–benzene (1 : 1) (4 l.). After being extracted once with saturated aqueous sodium hydrogen carbonate solution (1 l.) and washed with water (1 l.), the organic solvent was shaken with 1% sodium hydroxide (1 l.). The deep violet-purple aqueous layer was separated, and the pigment re-extracted into benzene (1 l.) by acidifying with 10% phosphoric acid. The benzene layer was washed once with water (500 c.c.), dried, and evaporated to dryness under reduced pressure. The solid residue was extracted (Soxhlet) with acetone–ethanol (1 : 1) (50 c.c.). On cooling, almost pure javanicin, m. p. 200° (450 mg.), separated. One recrystallisation from hot acetone–ethanol (1 : 1) (50 c.c.) yielded pure javanicin, m. p. 207—208° (decomp.). Method (*c*) was more convenient than (*a*) and gave consistent yields provided spore suspensions had been used for inoculating the medium. When inoculation was carried out by using a platinum loop, the yields were very variable, as shown below:

Vol. of filtered metabolism solution (l.)		20	20	20	40
Yield of pure pigment	Mg.	430	325	433	950
	Mg./l.	21·5	16·3	21·7	23·8

Javanicin when crystallised repeatedly from ethanol separated in red laths with a coppery lustre, m. p. 207·5—208° (decomp.). Analyses were carried out on different samples from several batches [Found: C, 62·1, 62·9, 61·8, 62·0, 62·4, 61·7; H, 4·95, 5·11, 4·92, 5·04, 5·11, 4·90. OMe, 10·4; side-chain Me (Kuhn–Roth), 9·2; active H, 0·98. $C_{15}H_{14}O_6$ requires C, 62·1; H, 4·86; 1 OMe, 10·7; 2 Me, 10·3; 3 H, 1·03%]. Light absorption in ethanol; $\lambda_{max.}$ 3030, 5050 A., log ε 3·97, 3·90; in chloroform, λ_{max} 3070, 5100 A., log ε 3·99, 3·86. Optical activity: A solution of javanicin (24·5 mg.) in acetone (50 ml.) in a 1-dm. tube showed no observable rotation.

Oxyjavanicin separated from chloroform or chloroform–light petroleum in clusters of red needles with a coppery lustre, m. p. 213—214° (decomp.; preheated bath) (Found: C, 58·6, 58·5; H, 4·65, 4·60; OMe, 9·9; side-chain Me, 5·3; active H, 0·79. $C_{15}H_{14}O_7$ requires C, 58·5; H, 4·61; OMe, 10·1; 1Me, 5·56; 2H, 0·66%). Light absorption: in chloroform, $\lambda_{max.}$ 3030, 5050 A., log ε 4·08, 3·96.

Monoacetylanhydrojavanicin.—(a) *From javanicin.* Javanicin (38 mg.) was dissolved in redistilled acetic anhydride (2·5 c.c.), and a trace of concentrated sulphuric acid added. There was an immediate darkening, and the mixture was heated at 100° for a few seconds till most of the red colour had disappeared, then poured into ice-cold distilled water (10 c.c.) and set aside for ½ hour; a yellow solid separated (yield, after drying in a vacuum, 26·3 mg.), m. p. 229—238° (decomp.). After two recrystallisations from ethanol the product formed long needles, m. p. 247—248° (decomp.) [Found, on different samples: C, 64·3, 65·05; H, 4·7, 4·6; OMe, 8·2, 9·3; *M* (cryoscopic in camphor), 317. $C_{16}H_{11}O_5(OMe)$ requires C, 64·9; H, 4·6, OMe, 9·85%; *M*, 314]. Light absorption: in ethanol, $\lambda_{max.}$ 2420, 2650, 3080, 3730 A., log ε 4·16, 4·20, 3·97, 3·59.

(b) *From anhydrojavanicin.* Anhydrojavanicin (29 mg.) was suspended in acetic anhydride (1 c.c.) containing a trace of concentrated sulphuric acid. On heating to 100° the colour changed to yellow. After 2 minutes the solution was poured on crushed ice (5 g.) and set aside for ½ hour, the yellow product separating in clusters of needles (28 mg.). After one crystallisation from ethanol, the m. p. was 249—250° (decomp.) alone and when mixed with javanicin anhydromonoacetate obtained above.

Anhydrojavanicin.—Javanicin (200 mg.) was suspended in dry ether (250 c.c.). Saturated ethereal hydrogen chloride (250 c.c.) was added, followed by anhydrous zinc chloride (0·5 g.). The mixture was shaken in a stoppered bottle for 3 hours, the colour having then changed to orange. The ethereal solution was washed several times with water till free from acid. The aqueous layer was washed with benzene (3 × 150 c.c.) to remove all the pigment. The benzene layer was combined with the ethereal solution, again washed with water (2 × 100 c.c.), and dried (Na_2SO_4). After removal of solvent, the solid residue was crystallised twice from acetone, from which it separated in clusters of needles, m. p. 244—245° (decomp.) (Found: C, 66·4; H, 4·50; active H, 0·53. $C_{15}H_{12}O_5$ requires C, 66·2; H, 4·42; one active H, 0·37%). Light absorption: in ethanol, $\lambda_{max.}$ 2300, 2640, 3160, 4500 A., log ε 4·49, 4·12, 3·95, 3·95. Javanicin (17 mg.) and concentrated sulphuric acid (1 c.c.) were heated together at 100° for 90 seconds. The solution was poured on crushed ice (10 g.), and a brown solid separated (20 mg.). The solid gave a violet coloration with 10% sodium hydroxide. It was dissolved in ethanol and reprecipitated by adding water, and then had m. p. 229—233° (decomp.). Repetition of this treatment yielded 1·3 mg. of a product which showed the following light absorption, in ethanol: $\lambda_{max.}$ 2350, 3160, 3240, 4560 A.; log ε (calculated for $M = 284$) 4·61, 3·92, 3·92, 3·91.

Javanicin Leucoanhydrotriacetate.—Anhydrojavanicin (250 mg.) in pyridine (20 c.c.) was warmed with acetic anhydride (2·5 c.c.). Zinc dust (1 g.) was added, and the reaction allowed to proceed for 5 minutes, the supernatant liquid then having become pale yellow. The solution was filtered and evaporated to small bulk. After a short time an almost colourless solid separated in rhombic prisms, m. p. 256—257° (decomp.) (321 mg., 87%). One recrystallisation from acetone–benzene afforded the pure *leucoanhydrotriacetate*, m. p. 258° (decomp.) (Found: C, 63·05; H, 5·10; CH_3·CO, 34·1. $C_{21}H_{20}O_8$ requires C, 63·0; H, 5·0; CH_3·CO, 32·25%). Light absorption in dioxan: $\lambda_{max.}$ 2610 A., log ε 4·92. Optical activity: A solution of 17·3 mg. in 2 ml. of chloroform in a 1-dm. tube showed no observable rotation.

Diacetyljavanicin.—Javanicin (50 mg.) was dissolved in pyridine (3 c.c.) and mixed with acetic anhydride (0·2 c.c.) in pyridine (2 c.c.). The solution was heated at 70° for 1 hour and kept at room temperature for a further 48 hours. After concentration to 1 c.c., a little ice was added which precipitated some gummy material. The supernatant liquid was decanted and further diluted with water (10 c.c.) and a yellow solid separated on cooling. The solid was crystallised from ethanol containing a little acetone. A second crystallisation from aqueous acetone yielded the pure *compound* (6·5 mg.) in clusters of needles, m. p. 207—208° (decomp.) (Found: C, 61·05; H, 4·95. $C_{19}H_{16}O_8$ requires C, 61·0; H, 4·81%). Light absorption, in ethanol: $\lambda_{max.}$ 2210, 2900, 4260 A., log ε 4·57, 4·17, 3·79.

Dibenzoyl Javanicin.—Javanicin (70 mg.), dissolved in pyridine (4 c.c.), was treated with benzoyl chloride (250 mg.). After about 10 minutes the red colour of the solution had changed to yellow. After a further 16 hours at room temperature, the solution was evaporated to dryness and the solid residue dissolved in ether–benzene (1 : 1) (25 c.c.). The solution was well washed with dilute hydrochloric acid (3 × 20 c.c.), followed by saturated aqueous sodium hydrogen carbonate (3 × 20 c.c.) and distilled water (20 c.c.). After drying (Na_2SO_4) the solvent was evaporated. The yellow residue was dissolved in ethanol (5 c.c.). On dilution with water (15 c.c.) some crystallisation took place, but most of the material was precipitated as a gum. On washing with cold ethanol, a pale yellow solid (47 mg.) was obtained. The *product* crystallised from hot ethanol–acetone (1 : 1) in bunches of needles, m. p. 216—217° (decomp.; preheated bath) (Found: C, 69·8; H, 4·41. $C_{33}H_{22}O_8$ requires C, 69·9; H, 4·42%). Light absorption in ethanol: $\lambda_{max.}$ 2290, 2600, 3650 A., log ε 4·63, 4·44, 3·52. Optical activity: A solution of 6·7 mg. in 2 ml. of chloroform in a 1-dm. tube showed no observable rotation.

Javanicin (29 mg.) was dissolved in N-sodium hydroxide (5 c.c.) and treated with sufficient iodine in potassium iodide to decolourise the solution completely. The solution had a strong smell of iodoform, and after standing at 0° overnight the precipitated iodoform was collected and dried (P_2O_5); yield 12·6 mg., m. p. 121—122° (decomp.) alone and when mixed with authentic iodoform.

Javanicin Mono-2 : 4-dinitrophenylhydrazone.—A hot solution of javanicin (25 mg.) in ethanol (3 c.c. and ethyl acetate (1 c.c.) was added to a cold solution of 2 : 4-dinitrophenylhydrazine, prepared by warming 2 : 4-dinitrophenylhydrazine (50 mg., 3 equivs.) with concentrated sulphuric acid (0·1 c.c.) till completely

dissolved, and diluting the cold solution with ethanol (1 c.c.). A red solid was immediately precipitated. The solution was warmed (100°) for a few seconds and cooled in ice. The solid was filtered off; yield 34 mg. (82%), m. p. 252—254° (decomp.; darkening at 249°). Recrystallisation from pyridine by adding ethanol yielded pure *javanicin mono-2 : 4-dinitrophenylhydrazone*, separating in needles, m. p. 255—256° (decomp.) (Found: C, 54·2, 53·4; H, 3·9, 3·7; N, 11·9. $C_{21}H_{18}O_9N_4$ requires C, 53·6; H, 3·83; N, 11·9%).

Monobromoanhydrojavanicin.—Anhydrojavanicin (50 mg.) was dissolved in chloroform (10 c.c.) and treated with excess of bromine in chloroform. The mixture was kept for 20 minutes at room temperature and evaporated to dryness. After being washed with a little ethanol, the residual solid was crystallised from benzene, from which it separated as tapered laths, m. p. 259—260° (decomp.) (yield 14 mg.). One recrystallisation from benzene–ethanol gave the pure *product*, m. p. 259—260° (decomp.) (Found: C, 51·35; H, 3·76. $C_{15}H_{11}O_5Br$ requires C, 51·3; H, 3·14%).

Acetoxyanhydroacetyljavanicin.—Javanicin (50 mg.) was refluxed for 15 minutes with acetic anhydride (5 c.c.) and anhydrous sodium acetate (50 mg.). The solution was poured on crushed ice, and the yellow solid filtered off after ½ hour. The solid was dissolved in acetone and reprecipitated with water; yield 14 mg. One recrystallisation from acetone–ethanol afforded the pure *compound*, m. p. 265° (extensive decomp.; darkening at 250°) (Found: C, 63·6; H, 4·8. $C_{19}H_{16}O_7$ requires C, 64·0; H, 4·5%).

We thank Sir Ian M. Heilbron, D.S.O., F.R.S., for his interest and encouragement, Dr. M. S. Lacey for bacteriological results, and the Medical Research Council and Rockefeller Foundation for financial assistance.

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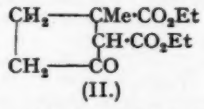
190. *The Course of Cyclisation in the Formation of Alicyclic Rings. Part I. Effect of Alkyl Groups on the Cyclisation of Esters of Polycarboxylic Acids.*

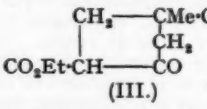
By R. N. CHAKRAVARTI.

The Dieckmann condensation of a simple or substituted β-alkyl-adipic or -pimelic ester leads to a ketonic ester in which the reactive methylene group nearer to the alkyl radical remains unaffected by preference when there is an alternative way of ring formation.

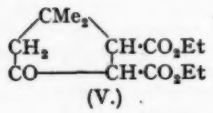
A DIFFICULTY often experienced in the synthesis of hydroaromatic ring systems is the determination of the structure of the ketonic esters obtained by the sodium condensation of esters of unsymmetrical polycarboxylic acids having two reactive methylene groups. A well-known example of this type is afforded by the sodium condensation of ethyl 2-methylbutane-1 : 2 : 4-tricarboxylate (I), which, on the basis of certain oxidative degradations, was found to lead to the keto-ester (II) (Baker, *J.*, 1931, 1548; cf. Banerjee, *J. Indian Chem. Soc.*, 1940, **17**, 423). More critical examination, however, revealed that the product of the condensation should be represented as ethyl 4-methyl*cyclo*pentanone-2 : 4-dicarboxylate (III) (Chakravarti, *J. Indian Chem. Soc.*, 1943, **20**, 173, 189, 243, 247, 399), and not (II) as was found by Baker (*loc. cit.*).

$CO_2Et{\cdot}CH_2{\cdot}CH_2{\cdot}CMe(CO_2Et){\cdot}\overset{*}{C}H_2{\cdot}CO_2Et$ (I.)

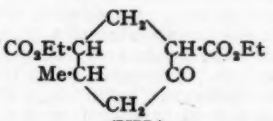

(II.)


(III.)

The cyclisation of the analogously constituted ethyl 2 : 2-dimethylbutane-1 : 3 : 4-tricarboxylate (IV) led to the keto-ester (V) (Perkin and Thorpe, *J.*, 1906, **89**, 781). Also, only (VII) was isolated in the cyclisation of ethyl 2-methylpentane-1 : 3 : 5-tricarboxylate (VI) (Chakravarti, *J. Indian Chem. Soc.*, 1944, **21**, 322).*


(V.)

$CO_2Et{\cdot}\overset{*}{C}H_2{\cdot}CMe_2{\cdot}CH(CO_2Et){\cdot}CH_2{\cdot}CO_2Et$ (IV.)


(VII.)

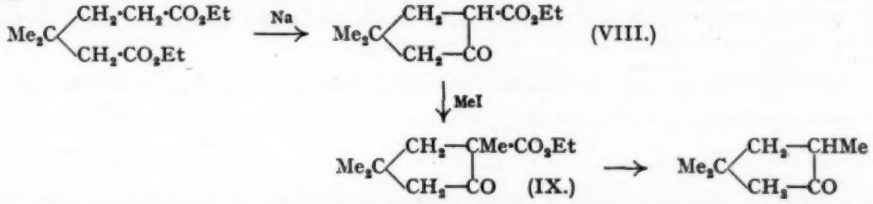
(VI.) $CO_2Et{\cdot}\overset{*}{C}H_2{\cdot}CHMe{\cdot}CH(CO_2Et){\cdot}CH_2{\cdot}CH_2{\cdot}CO_2Et$

The above results definitely lead one to believe that the methyl groups in (I), (IV), and (VI) exert some steric influence on the reactive methylene groups marked (*), which accounts for

* Since this paper was communicated, another interesting case has been discussed elsewhere (Chakravarti, *Experientia*, 1947, **3**, 149).

their lesser reactivity. This effect may be due to the positive character of the alkyl group, and if this be true it can be concluded that the positive character of a methyl group is much more pronounced than the negative character of a carbethoxyl group (cf. the first example cited above).

In the present instance, while devising a suitable method for the synthesis of 4 : 4-dimethyl-*cyclo*pentanone-2-acetic acid required in connection with another work, it became necessary to investigate the action of sodium on ethyl ββ-dimethyladipate. For this purpose, the product of the sodium condensation was heated with excess of methyl iodide and the resulting methylated keto-ester hydrolysed with dilute aqueous alkali to give a neutral ketone, b. p. 160°. It gave a crystalline semicarbazone, m. p. 168°, which proved to be identical with that of 2 : 4 : 4-trimethyl*cyclo*pentanone (Wallach, *Annalen*, **1918**, **414**, 331; Qudrat-i-Khuda, *Nature*, **1933**, **132**, 210; Dey and Linstead, *J.*, **1935**, 1063). No evidence of the presence, in the hydrolysed product, of the isomeric ketone, 2 : 3 : 3-trimethyl*cyclo*pentanone (von Kregten, *Rec. Trav. chim.*, **36**, 78; Noyes, *Ber.*, **1899**, **32**, 2291), b. p. 167—169° (semicarbazone, m. p. 222°), could be detected, thus indicating that in this cyclisation the keto-ester (VIII) is the only product.



The result obtained above confirms the view already postulated that the reactivity of a methylene group is reduced considerably by its closer proximity to a methyl group (or any other alkyl group). Thus the action of sodium on the ester of a substituted β-alkyl-adipic or -pimelic acid (having two alternatives for cyclisation) may be expected to lead to a ketonic ester in which the reactive methylene group, nearer to the alkyl radical, remains unaffected by preference. The other isomer in such a case, if produced at all, can only be in much smaller amount. This view is also in line with the results obtained by the cyclisation of ethyl β-methyl-adipate (Dieckmann and Groeneveld, *Ber.*, **1900**, **33**, 595) and -pimelate (Einhorn and Klages, *ibid.*, **1901**, **34**, 3793).

Experimental.

ββ-Dimethyladipic acid, required for this work, was prepared by the improved method of Rydon (*J.*, 1936, 594; 1937, 1341).

Ethyl 2 : 4 : 4-*Trimethyl*cyclo*pentanone*-2-*carboxylate* (IX).—Ethyl ββ-dimethyladipate (20 g.) was heated on the water-bath with a fine suspension of sodium (3·9 g.) in anhydrous benzene (50 c.c.) The heating was continued for about 6 hours till the whole of the sodium had passed into solution. The product was then cooled in ice, treated with excess of methyl iodide (20 c.c.), and kept overnight. The methylation was completed by heating the reaction mixture on the water-bath for 5—6 hours. The product at this stage should not give any coloration with alcoholic ferric chloride. Sufficient water was added to dissolve the sodium iodide, and the benzene layer was separated. It was washed thoroughly with water and dried ($CaCl_2$), and the solvent evaporated. The residual liquid on distillation under reduced pressure gave the *ester* as a colourless mobile oil (12 g.) with a characteristic odour, b. p. 88°/4 mm. (Found : C, 66·5; H, 9·1. $C_{11}H_{18}O_3$ requires C, 66·7; H, 9·1%).

2 : 4 : 4-*Trimethyl*cyclo*pentanone*.—The above ketonic ester (11·5 g.) was heated on a sand-bath for 6 hours with a solution of potassium hydroxide (12 g.) in water (150 c.c.). When cold, the product was taken up in ether, washed well with water, and dried (Na_2SO_4), and the ether removed. The liquid remaining was then distilled; with the exception of a little high boiling residue, it came over constantly at 160°, as a colourless liquid (6·8 g.) with a peppermint-like smell (Found : C, 75·9; H, 11·2. Calc. for $C_8H_{14}O$: C, 76·2; H, 11·1%). With semicarbazide acetate in aqueous alcohol it readily gave a semicarbazone, which crystallised from spirit in colourless shining laminæ, m. p. 168°, undepressed in admixture with an authentic specimen of the semicarbazone of 2 : 4 : 4-trimethyl*cyclo*pentanone (Found : C, 59·2; H, 9·4. Calc. for $C_9H_{17}ON_3$: C, 59·0; H, 9·3%).

Further work with 4 : 4-dimethyl*cyclo*pentanone-2-acetic acid is in progress.

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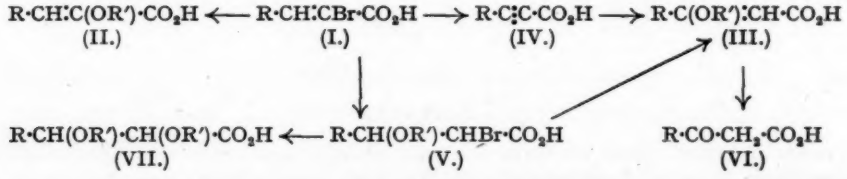
191. *Olefinic Acids. Part II. The Reactivity of α-Bromoacrylic Acid and Some Related Compounds.*

By L. N. Owen and H. M. Babatunde Somade.

α-Bromoacrylic acid reacts with alkoxides to give α-bromo-β-alkoxy-propionic acids which, by further action, are converted into β-alkoxy-acrylic and αβ-dialkoxy-propionic acids, the proportion of β-alkoxy-acid being greater when the higher alkoxides are used. In contrast with the results obtained in the crotonic series (Part I), no α-alkoxy-acrylic acids are formed. Towards thioacetic acid, benzylthiol, diazomethane, and methyl diazoacetate, the order of decreasing reactivity is, as would be anticipated, α-bromoacrylic acid, α-bromocrotonic acid, α-bromo-ββ-dimethylacrylic acid; the products obtained by these addition reactions have been investigated and identified.

The absorption spectra of several α- and β-alkoxy-acrylic acids are recorded.

The investigations described in Part I (Owen, *J.*, 1945, 385) established that α-bromocrotonic acid (I; R = Me) reacted with alkoxides (or the appropriate alcoholic alkali) to give α- and β-alkoxy-crotonic acids, (II; R = Me) and (III; R = Me), the proportion of the latter being greater with the higher alkoxides, but attempts to isolate either of the possible intermediates (IV) or (V) were unsuccessful.



Baker (*J.*, 1942, 520) in the course of attempts to prepare α-alkoxy-acrylic acids, has shown that αβ-dibromopropionic acid, on treatment with boiling methanolic sodium methoxide, yields αβ-dimethoxypropionic acid, not by direct substitution, but probably *via* α-bromoacrylic acid. The presence of other products was indicated by the unsaturated nature of the crude halogen-free acids isolated from the reaction mixture, but these were not identified, and the exact mechanism of the reaction was not established. It has now been found that β-*methoxyacrylic acid* is formed under these conditions; on cold acid hydrolysis it gives malonic semi-aldehyde (VI; R = H) (2 : 4-*dinitrophenylhydrazone*, m. p. 136°).

The reaction has been more closely studied by using α-bromoacrylic acid (I; R = H) as starting material, particularly with a view to comparing its behaviour with that of α-bromocrotonic acid. When boiled with methanolic sodium methoxide for 3 hours, the main product was α-bromo-β-methoxypropionic acid (V; R = H, R′ = Me), which was isolated as its methyl ester, purified from unsaturated compounds by cautious treatment with aqueous permanganate, and characterised as the amide, m. p. 83°. The presence also of a small amount of β-methoxyacrylic acid (III; R = H, R′ = Me) was demonstrated by the formation of malonic semi-aldehyde by acid hydrolysis of a portion of the reaction products. No α-methoxyacrylic acid could be detected, but, clearly, if it had been formed it might well have been converted by subsequent reaction with methanol into αβ-dimethoxypropionic acid. This, however, has been shown not to be the case, since, by saponification of methyl α-methoxyacrylate, crystalline *α-methoxyacrylic acid*, m. p. 52°, was obtained,* which was recovered unchanged after treatment with boiling methanolic sodium methoxide; β-methoxyacrylic acid, treated similarly, was likewise unaffected.

It is evident, therefore, that α-bromoacrylic acid, in marked contrast to α-bromocrotonic acid, undergoes addition, rather than substitution, and gives the bromomethoxy-acid (V; R = H, R′ = Me), the bromine atom in which is then either eliminated as hydrogen bromide, forming β-methoxyacrylic acid (III; R = H, R′ = Me), or replaced to give αβ-dimethoxypropionic acid (VII; R = H, R′ = Me).

It was not possible to interrupt the reaction of α-bromoacrylic acid with ethanolic alkali at the bromo-ethoxy-acid stage, probably owing to the heterogeneous nature of the reaction mixture resulting from the reduced solubility of the salts in ethanol, but on taking the reaction to com-

* Allpress and Haworth (*J.*, 1924, **125**, 1233) tentatively ascribed this structure to an unsaturated liquid acid, b. p. 65—75°/12 mm., obtained by the action of methyl chloroformate on fructose; it is possible that their product was an impure form of α-methoxyacrylic acid, although no other properties were given in support of the proposed constitution.

pletion β-ethoxyacrylic acid was obtained, together with αβ-diethoxypropionic acid, isolated as the *ethyl* ester. Treatment of α-bromoacrylic acid with potassium *iso*propoxide gave a liquid product, containing 88% of β-iso*propoxyacrylic acid* with 12% of αβ-di*iso*propoxypropionic acid, which could not be separated, whilst with potassium *tert.*-butoxide the only product isolated was crystalline β-tert.-*butoxyacrylic acid*. This progressive increase in the proportion of the β-alkoxy-acid as the higher alkoxides are used is similar to that observed in the case of α-bromocrotonic acid; in the present reactions, however, the increase is at the expense of dialkoxypropionic acid, whilst in the crotonic series it is accompanied by a diminution in the amount of α-alkoxy-acid.

The absorption data for the α- and β-alkoxy-acrylic acids are shown in the table. As was observed in the crotonic series (Owen, *loc. cit.*) the β-compounds absorb more strongly than their α-isomerides, but in contrast, not at appreciably different wave-lengths.

Light Absorption of Alkoxy-acrylic Acids in Alcohol.

	$\lambda_{max.}$, A.	$\epsilon_{max.}$		$\lambda_{max.}$, A.	$\epsilon_{max.}$
α-Methoxy	2280	6000	β-Methoxy	2280	14,100
α-Ethoxy *	2290	7000	β-Ethoxy	2300	14,700
	2360 †	6150			
			β-*iso*Propoxy	2340	14,000 ‡
			β-*tert.*-Butoxy	2370	15,400

* M. p. 61°, prepared by the method of Claisen (*Ber.*, 1898, **31**, 1019; cf. von Auwers, *ibid.*, 1911, **44**, 3524).

† Inflection. ‡ Corrected value.

The greater ease of addition to α-halogeno-acrylic, as compared with α-halogeno-crotonic, acids has also been demonstrated in their reactions with a number of other reagents. α-Bromoacrylic acid reacted readily with thioacetic acid to give α-*bromo*-β-(*acetylthio*)*propionic acid* (VIII); the corresponding *chloro*-acid was obtained similarly. α-Bromocrotonic acid failed to undergo addition of the reagent, thus indicating that diminution of ethenoid activity is brought about not only by the methyl group in the β-position, but also by the halogen atom, since crotonic acid undergoes the reaction (Holmberg and Schjanberg, *Arkiv Kemi, Min. Geol.*, 1940, **14** *A*, No. 7, 22).

With benzylthiol in pyridine solution, α-bromoacrylic acid gave β-(*benzylthio*)*acrylic acid* (IX), presumably *via* the intermediate compound (X); α-bromocrotonic acid could not be induced to react with the reagent.

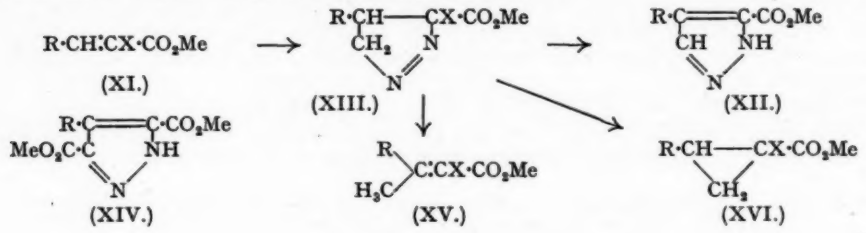
$CH_2(SAc)\cdot CHBr\cdot CO_2H$ (VIII.) $CH_2(SBz)\cdot CHBr\cdot CO_2H$ (X.) $CH(SBz):CH\cdot CO_2H$ (IX.)

Auwers and Kōnig (*Annalen*, 1932, **496**, 31) reported that methyl α-chlorocrotonate (XI; R = Me, X = Cl) reacted with diazomethane to give methyl 4-methylpyrazole-3-carboxylate (XII; R = Me), hydrogen chloride being spontaneously evolved by the unstable intermediate (XIII; R = Me, X = Cl). It has now been shown that α-chloro- and α-bromo-acrylic acids, on treatment with diazomethane, give methyl pyrazole-3-carboxylate (XII; R = H), whilst α-bromocrotonic acid gives (XII; R = Me). α-Bromo-ββ-dimethylacrylic acid, on the contrary, was merely converted into its *methyl* ester (*amide*, m. p. 129°) and did not undergo addition, the extra methyl group in the β-position being sufficient to inhibit the reaction.

Buchner and Papandieck (*Annalen*, 1893, **273**, 246), by treatment of methyl αβ-dibromopropionate with methyl diazoacetate, obtained dimethyl pyrazole-3 : 5-dicarboxylate (XIV; R = H), but did not isolate any of the intermediates. Both methyl α-bromo- and α-chloroacrylate have now been found to give this product under these conditions, whilst methyl α-bromo- and α-chloro-crotonates reacted much less readily, and gave a small yield of *methyl 4-methylpyrazole-3 : 5-dicarboxylate* (XIV; R = Me). Methyl α-bromo-ββ-dimethylacrylate was unaffected by methyl diazoacetate.

In the reaction of diazomethane with α-substituted acrylic or crotonic esters (XI), provided that the intermediate pyrazoline (XIII) does not tend to lose HX and form pyrazoles (cf. above), it may lose nitrogen to give either a higher homologue (XV) of the ester (XI) or a *cyclo*propane derivative (XVI). The composition of the product depends on the nature of the substituent X; if it is methyl, both (XV)and (XVI) are obtained, whilst if X is a cyano- or carbalkoxy-group the sole product is (XV) (Auwers and König, *Annalen*, 1932, **496**, 252; Young, Andrews, Lindenbaum, and Cristol, *J. Amer. Chem. Soc.*, 1944, **66**, 810). It was therefore not unexpected to find that methyl α-methoxyacrylate (XI; R = H, X = OMe) on reaction with diazomethane

gave a product which contained methyl 1-methoxy*cyclo*propane-1-carboxylate (XVI; R = H, X = OMe), characterised as the *amide*, m. p. 117°. This $+T$ effect of the methoxyl group in the α-position was also shown by the observation that although, as mentioned above, methyl α-methoxyacrylate was unaffected by methanolic sodium methoxide, it reacted with methanolic hydrogen chloride to give methyl αα-dimethoxypropionate.



Experimental.

Action of Sodium Methoxide on αβ-Dibromopropionic Acid.—To the acid (24 g.) in warm methanol (20 c.c.) was added methanolic sodium methoxide (110 c.c., 3·76 N). After the vigorous reaction had subsided, the mixture was refluxed for 7 hours, during which the suspension of potassium α-bromoacrylate disappeared and was replaced by a granular precipitate of potassium bromide. After removal of solvent, the residue was dissolved in water and acidified with hydrochloric acid, with ice-cooling. Extraction with ether gave a syrup, which partly crystallised on standing. The solid *β-methoxyacrylic acid* (1·1 g.) was dried on porous tile; it recrystallised from water in plates, m. p. 102° (Found: C, 47·2; H, 5·9; equiv., 102. $C_4H_6O_3$ requires C, 47·1; H, 5·9%; equiv., 102). Light absorption: see Table. On treatment with a cold solution of 2 : 4-dinitrophenylhydrazine sulphate in 5N-sulphuric acid for 2 hours it gave the 2 : 4-*dinitrophenylhydrazone* of malonic semi-aldehyde, which crystallised from warm ethyl acetate–light petroleum (b. p. 40—60°) in lemon-yellow nodules, m. p. 136° (decomp.), and gave a deep red solution in aqueous sodium hydroxide (Found: C, 40·0; H, 3·3; N, 20·6. $C_9H_8O_6N_4$ requires C, 40·3; H, 3·0; N, 20·9%).

α-Bromoacrylic Acid.—αβ-Dibromopropionic acid (90 g.) was dissolved in water and neutralised with N-sodium hydroxide at 0°. An equal volume of N-sodium hydroxide was then added and the solution left at room temperature for 1 hour. After acidification with a slight excess of concentrated hydrochloric acid (Congo-red), ether extraction yielded α-bromoacrylic acid, which after recrystallisation from light petroleum (b. p. 60—80°) formed colourless prisms (51 g., 87%), m. p. 72° (lit. 70°). This improved procedure gives a product which, unlike less pure material, shows no sign of decomposition after being kept for several months.

Reaction of α-Bromoacrylic Acid with Alkoxides.—(i) A solution of the acid (15 g.) in methanol (40 c.c.) was treated with methanolic sodium methoxide (35 c.c., 3·67N) and refluxed for 3 hours, after which it was evaporated to dryness, and the residue dissolved in water, acidified with hydrochloric acid, and extracted with ether. The liquid acid so obtained contained a small amount of β-methoxyacrylic acid, since a portion, on treatment with aqueous 2 : 4-dinitrophenylhydrazine sulphate, gave the 2 : 4-dinitrophenylhydrazone of malonic semi-aldehyde, m. p. 135°. The remainder (7 g.) was dissolved in methyl iodide (5 c.c.) and diluted with ether (10 c.c.), and silver oxide (15 g.) was added in small portions during ½ hour. After refluxing for ½ hour, the solution was filtered and evaporated to an oil, which on distillation furnished a main fraction (6·1 g.), b. p. 70—78°/15 mm. This was unsaturated towards alkaline permanganate, and gave a positive reaction on standing with aqueous 2 : 4-dinitrophenylhydrazine sulphate. It was therefore suspended in dilute sodium carbonate solution and treated with a slight excess of 2% aqueous potassium permanganate at 0°, with vigorous stirring. The recovered saturated ester (3·0 g.), b. p. 78°/15 mm., $n_D^{19°}$ 1·4510, was mainly methyl α-bromo-β-methoxypropionate, probably containing a small amount of methyl αβ-dimethoxypropionate (Found: C, 33·4; H, 5·7. Calc. for $C_5H_9O_3Br$: C, 30·5; H, 4·6. Calc. for $C_6H_{12}O_4$: C, 48·6; H, 8·2%). On treatment with aqueous ammonia (*d* 0·880) it gave α-bromo-β-methoxypropionamide, m. p. 83° (Found: C, 26·2; H, 4·5. Calc. for $C_4H_8O_2NBr$: C, 26·4; H, 4·4%).

(ii) Ethanolic sodium ethoxide (45 c.c., 2N) was added to α-bromoacrylic acid (10 g.) in ethanol (10 c.c.) and the mixture was refluxed for 20 hours. The residue, after removal of solvent, was dissolved in water and acidified with hydrochloric acid, precipitating β-ethoxyacrylic acid (1·0 g.), which crystallised from warm water in plates, m. p. 109°. Light absorption: see Table. Ether extraction of the residual aqueous portion gave a liquid halogen-free acid (5·1 g.), which was esterified in the usual way in ethereal solution with ethyl iodide and silver oxide. The crude ester was then purified by treatment with 2% potassium permanganate, as already described, and on distillation gave *methyl αβ-diethoxypropionate* (1·5 g.), b. p. 87°/11 mm., $n_D^{21°}$ 1·4130 (Found: C, 56·8; H, 9·8. $C_9H_{18}O_4$ requires C, 56·8; H, 9·5%).

(iii) α-Bromoacrylic acid (7·5 g.), dissolved in *iso*propanol (60 c.c.), was treated with a solution of potassium (5 g.) in *iso*propanol (60 c.c.), and the semi-solid mass was refluxed for 24 hours on the steam-bath. The solvent was then removed, and the residue dissolved in water and acidified with hydrochloric acid; an oil separated, but since it could not be induced to crystallise, the whole was extracted with ether. The liquid acid so obtained (7 g.), b. p. 55°/0·001 mm., $n_D^{15°}$ 1·4425, contained no halogen and was highly unsaturated. Light absorption: $\lambda_{max.}$ 2340 A. (ϵ 12,300) (Found: equiv., 137. $C_6H_{10}O_3$ requires equiv., 130. $C_8H_{14}O_4$ requires equiv., 190). On treatment with aqueous 2 : 4-dinitrophenylhydrazine sulphate it gave the 2 : 4-dinitrophenylhydrazone of malonic semi-aldehyde, m. p. 129° (decomp.) after recrystallisation from dioxan, and was therefore mainly *β-iso*propoxyacrylic acid, probably containing

ca. 12% αβ-di*iso*propoxyacrylic acid. Attempts to isolate either component in a pure state were unsuccessful.

(iv) To a warm solution of potassium (10 g.) in *tert.*-butanol (200 c.c.) was added α-bromoacrylic acid (15·2 g.) in *tert.*-butanol (20 c.c.), and the semi-solid mass refluxed for 24 hours on the steam-bath. Water (100 c.c.) was then added and the *tert.*-butanol removed under reduced pressure. The residual aqueous solution was acidified to Congo-red with hydrochloric acid, which precipitated *β-tert.-butoxyacrylic acid* (3·2 g.); this was collected, and a further quantity (1·7 g.) obtained by extraction of the filtrate with ether. On recrystallisation from light petroleum (b. p. 60—80°) it formed long flat needles, m. p. 86·5° (Found: C, 58·6; H, 8·5; equiv., 144. $C_7H_{12}O_3$ requires C, 58·3; H, 8·4%; equiv., 144). Light absorption: see Table. On standing with aqueous 2 : 4-dinitrophenylhydrazine sulphate it gave the 2 : 4-dinitrophenylhydrazone of malonic semi-aldehyde, m. p. 131°. No other acidic products could be detected.

α-Methoxyacrylic Acid.—Methyl α-methoxyacrylate, b. p. 58—60°/15 mm., $\lambda_{max.}$ 2280 A. (ε 7300), $\lambda_{inf.}$ 2360 A. (ε 6400), was prepared by the method of Baker (*loc. cit.*). The ester (2·1 g.) was heated at 100° with aqueous sodium hydroxide (15 c.c., 2N) for 1½ hours, and the solution then cooled, acidified with 2N-hydrochloric acid (15 c.c.), and extracted with ether. Evaporation of the dried extract gave *α-methoxyacrylic acid* (1·2 g.), which crystallised from light petroleum (b. p. 40—60°) in needles, m. p. 52° (Found: C, 46·8; H, 5·7. $C_4H_6O_3$ requires C, 47·0; H, 5·9%). Light absorption: see Table. On standing with aqueous 2 : 4-dinitrophenylhydrazine sulphate it gave the 2 : 4-dinitrophenylhydrazone of pyruvic acid, m. p. 218°.

Action of Sodium Methoxide on α-Methoxy- and β-Ethoxy-acrylic Acids.—α-Methoxyacrylic acid (0·2 g.) was refluxed with methanolic sodium methoxide (3 c.c., N) for 6 hours. After evaporation, acidification of the residue with hydrochloric acid and extraction with ether, the acid (0·17 g.), m. p. and mixed m. p. 50°, was recovered unchanged. β-Ethoxyacrylic acid (0·25 g.), treated similarly, was also recovered (0·21 g.), m. p. and mixed m. p. 108°.

α-Bromo-β-(acetylthio)propionic Acid.—α-Bromoacrylic acid (5 g.) was added in small portions to thioacetic acid (5 c.c.) in a flask cooled in ice. After the vigorous reaction had subsided, the solution was heated on the steam-bath for 15 minutes, and the excess of thioacetic acid then removed under reduced pressure. The solid *acid* obtained on cooling was recrystallised from carbon tetrachloride, from which it formed colourless prisms (6·9 g.), m. p. 85—86° (Found: C, 26·1; H, 3·2. $C_5H_7O_3SBr$ requires C, 26·4; H, 3·1%). Similar treatment of α-chloroacrylic acid (2 g.) afforded *α-chloro-β-(acetylthio)propionic acid* (3 g.), m. p. 75°, after recrystallisation from carbon tetrachloride (Found: C, 32·8; H, 3·75. $C_5H_7O_3ClS$ requires C, 32·9; H, 3·9%). Under the same conditions, α-bromocrotonic acid was recovered unchanged.

Action of Benzylthiol on α-Bromoacrylic Acid.—The acid (0·5 g.), pyridine (0·5 c.c.), and benzylthiol (1 c.c.) were heated on a steam-bath for 15 minutes. The solid which separated on cooling was freed from adhering oil on porous tile, dissolved in dilute hydrochloric acid, and extracted with ether. Removal of solvent yielded *β-(benzylthio)acrylic acid*, which crystallised from carbon tetrachloride in colourless plates, m. p. 162—163° (Found: C, 61·45; H, 5·3. $C_{10}H_{10}O_2S$ requires C, 61·8; H, 5·2%. Light absorption: $\lambda_{max.}$ 2740 A. (ε 15,500). Similar experiments, in which traces of hydrochloric acid or benzoyl peroxide were used in place of pyridine, resulted only in the recovery of unchanged bromo-acid.

Reactions of α-Halogeno-αβ-olefinic Acids with Diazomethane.—(i) α-Bromoacrylic acid (2 g.) was dissolved in excess of ethereal diazomethane and left at 20° for 5 days. After removal of solvent, the liquid residue was warmed to 60°, whereupon there was a vigorous evolution of hydrogen bromide and the formation of methyl pyrazole-3-carboxylate, which crystallised from water in colourless prisms (0·9 g.), m. p. 141° (Found: C, 47·6; H, 4·7; N, 22·3. Calc. for $C_5H_6O_2N_2$: C, 47·6; H, 4·8; N, 22·2%). α-Chloroacrylic acid under identical conditions gave the same product, m. p. 141°.

(ii) α-Bromocrotonic acid (1 g.) treated similarly, gave methyl 4-methylpyrazole-3-carboxylate (0·51 g.), colourless prisms from water, m. p. 170° (Found: C, 51·2; H, 5·75; N, 19·8. Calc. for $C_6H_8O_2N_2$: C, 51·05; H, 5·7; N, 19·85%).

(iii) α-Bromo-ββ-dimethylacrylic acid (2 g.) was dissolved in excess of ethereal diazomethane and the solution kept at 20° for 12 days. Removal of solvent afforded a nitrogen-free product (1·8 g.), b. p. 98°/33 mm., which was identical with *methyl α-bromo-ββ-dimethylacrylate*, b. p. 76°/9 mm., $n_D^{21°}$ 1·4909 (Found: C, 37·8; H, 4·8. $C_6H_9O_2Br$ requires C, 37·3; H, 4·7%), prepared by esterification of the bromo-acid with methanol and sulphuric acid, since both specimens with aqueous ammonia (*d* 0·880) gave *α-bromo-ββ-dimethylacrylamide*, needles from light petroleum (b. p. 60—80°), m. p. and mixed m. p. 129° (Found: C, 34·0; H, 4·7; N, 7·5. C_5H_8ONBr requires C, 33·7; H, 4·5; N, 7·9%).

Reactions of Methyl α-Bromo-αβ-olefinic Esters with Methyl Diazoacetate.—(i) A solution of methyl α-bromoacrylate (1 g.) and methyl diazoacetate (2 g.) in light petroleum (b. p. 80—100°) (50 c.c.) was refluxed for 15 hours (during which the intensity of the deep yellow colour was much reduced) and then evaporated to dryness under reduced pressure. The solid residue of methyl pyrazole-3 : 5-dicarboxylate (1·3 g.) crystallised from water in colourless prisms, m. p. 152° (Found: N, 15·3. Calc. for $C_7H_8O_4N_2$: N, 15·2%). The same product (0·6 g.), m. p. 152°, was also obtained from methyl α-chloroacrylate (1 g.).

(ii) A solution of methyl α-bromocrotonate (1 g.) and methyl diazoacetate (1 g.) in light petroleum (b. p. 80—100°) (25 c.c.) after refluxing for 24 hours was still deeply coloured, in spite of the use of the excess of bromo-ester. Evaporation under reduced pressure gave a small residue of *methyl 4-methylpyrazole-3 : 5-dicarboxylate*, colourless prisms (0·15 g.) from water, m. p. 128—129° (Found: C, 48·85; H, 5·2; N, 14·0. $C_8H_{10}O_4N_2$ requires C, 48·5; H, 5·1; N, 14·1%), which was also obtained, in similar yield, from methyl α-chlorocrotonate under the same conditions.

(iii) A solution of methyl α-bromo-ββ-dimethylacrylate (1 g.) and methyl diazoacetate (1 g.) in light petroleum (b. p. 80—100°) (20 c.c.) was refluxed for 4 days, after which the solvent and diazo-ester were removed under reduced pressure. The residual nitrogen-free liquid, b. p. 70°/6 mm., was unchanged bromo-ester, identified by conversion into the amide, m. p. and mixed m. p. 128°.

Action of Diazomethane on Methyl α-Methoxyacrylate.—The methoxy-ester (1 g.) was treated with

excess of ethereal diazomethane at 20° for 4 days. Removal of solvent gave a liquid, b. p. *ca.* 135°, which by treatment with aqueous ammonia (*d* 0·880) was converted into 1-*methoxy*cyclo*propane*-1-*carboxyamide*; this crystallised from light petroleum (b. p. 40—60°) in colourless needles, m. p. 117°, which showed no unsaturation towards alkaline permanganate (Found: C, 52·2; H, 8·0; N, 11·9. $C_5H_9O_2N$ requires C, 52·2; H, 7·9; N, 12·2%).

Action of Methanolic Hydrogen Chloride on Methyl Methoxyacrylate.—The methoxy-ester (1 g.) was dissolved in methanol (5 c.c.) and saturated with dry hydrogen chloride at 0°. After ½ hour, the hydrogen chloride was removed by aeration and finally by neutralisation with barium carbonate. Evaporation of the solvent and extraction of the residue with ether gave methyl αα-dimethoxypropionate, b. p. 67°/20 mm., which on treatment with methanolic 2 : 4-dinitrophenylhydrazine sulphate gave the 2 : 4-dinitrophenylhydrazone of methyl pyruvate, m. p. 186—187°; it was also characterised by conversion, with aqueous ammonia, into αα-dimethoxypropionamide, m. p. 117° (Found: N, 10·5, Calc. for $C_5H_{11}O_3N$: N, 10·5%).

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192. *Tetrahydroacridones and Related Compounds as Antimalarials.*

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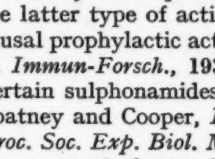
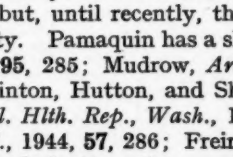
Tetrahydroacridones, 12-hydroxydihydro-β-quinindenes, and 2- and 4-hydroxyquinolines have been examined for antimalarial activity. Marked prophylactic action has been found against *P. gallinaceum* infections in chicks and the structural requirements for activity are outlined. The experimental conditions for the Conrad–Limpach ring-closure of β-arylamino-$\Delta^{\alpha\beta}$-unsaturated esters are discussed.

THERE are two approaches to the chemotherapy of malaria. The prophylactic approach aims at rendering the bite of the mosquito ineffective in producing an infection and the therapeutic approach aims at the eradication of an established infection; the former is directed at the sporozoites injected by the mosquito and the subsequent (primary) tissue phase development, while the latter aims at control during the later erythrocytic stages in the developmental cycle of the parasite. Quinine, mepacrine, and pamaquin, to which paludrine and several 4-dialkylaminoalkylaminoquinolines may now be added, are well-established examples of drugs possessing the latter type of action but, until recently, there have been few reports of drugs exhibiting causal prophylactic activity. Pamaquin has a slight prophylactic action (Kikuth and Mudrow, *Z. Immun-Forsch.*, 1939, **95**, 285; Mudrow, *Arch. Schiffs- u. Tropen-Hygiene*, 1940, **44**, 257). Certain sulphonamides (Sinton, Hutton, and Shute, *Ann. Trop. Med. Parasit.*, 1939, **33**, 37; Coatney and Cooper, *Publ. Hlth. Rep., Wash.*, 1944, **59**, 1455; Coggeshall, Porter, and Laird, *Proc. Soc. Exp. Biol. Med.*, 1944, **57**, 286; Freire and Paraense, *Rev. Brasil. Biol.*, 1944, **4**, 27) have a marked causal prophylactic action, as does paludrine (Curd, Davey, and Rose, *Ann. Trop. Med. Parasit.*, 1945, **39**, 208), while *p*-methylsulphonylbenzamidine (Fuller, Tonkin, and Walker, *J.*, 1945, 633) and some arylguanidines (King and Tonkin, *J.*, 1946, 1063) have a slight effect. When the war in Europe ended, reports came to hand (Fitch, *Pharm. J.*, 1945, **155**, 182; *Combined Intelligence Objectives Sub-Committee*, 1945, Item No. 24, File No. XXIII–12; *idem*, File No. XXIV–20; *idem*, File No. XXV–54) that German workers had encountered causal prophylactic activity in certain 4-hydroxyquinolines, notably 4-hydroxy-7-methoxy-3-*n*-heptylquinaldine (I) (endochin), and the present authors at once recorded, in a preliminary way, similar observations with a chemically related series (*Nature*, 1945, **156**, 629); the present paper describes this work in detail.

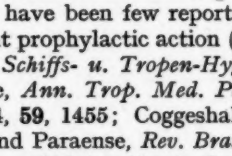
An examination of a number of tetrahydroacridones (II), 12-hydroxy-2 : 3-dihydro-β-quinindenes (III) (for numbering, see Blount, Perkin, and Plant, *J.*, 1929, 1976), and 2- and 4-hydroxyquinolines for causal prophylactic activity in *Plasmodium gallinaceum* infections in chicks revealed definite activity in compounds conforming to type (IV), of which (I), (II), and



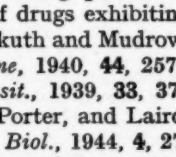
(I.)



(II.)



(III.)



(IV.)

(III) are representative, R′ and R″ being saturated hydrocarbon residues. For example, 3-methoxyacridone showed no activity while its tetrahydro-derivative, 7-methoxy-1 : 2 : 3 : 4-

tetrahydroacridone (V), was the most active substance encountered, being, on a weight basis, about twice as active as sulphadiazine and four times as active as endochin (I), our investigations being ultimately extended to include comparison with this substance. Access to compounds of types (II), (III), and (IV) was obtained by condensation of the appropriate aromatic primary amines and β-keto-esters, followed by thermal cyclization of the resulting β-arylamino-$\Delta^{\alpha\beta}$-unsaturated esters. This reaction was described first for ethyl acetoacetate by Conrad and Limpach (*Ber.*, 1887, **20**, 944) who simply heated the intermediate products to about 250° and rarely obtained yields greater than 30%. The reaction was used by numerous workers in the interval and many years elapsed before Limpach (*Ber.*, 1931, **64**, 969; D.R.-P. 455,387) made the significant improvement of effecting ring-closure by adding the intermediate products to liquid paraffin preheated to 250—280° and claimed yields of over 90%. Our own experience has been that decomposition is frequently excessive under Limpach's conditions as the products separate on the walls of the reaction vessel and there become overheated, and the yields are not as good as those claimed; other criticisms have been advanced by Maurin (*Ann. Chim.*, 1935, **4**, 309). Ashley *et al.* (*Proc. Roy. Soc.*, 1933, *B*, **113**, 295) used molten paraffin wax which was subsequently removed by a solvent. It was obvious to us that the best thermal control and mixing could be obtained by using a vigorously boiling inert solvent of suitable boiling point. For several years, therefore, we have used vigorously boiling diphenyl (b. p. 255°) for this purpose and have obtained clean products in good yield thereby; American workers (Price and Roberts, *J. Amer. Chem. Soc.*, 1946, **68**, 1204; Steck, Hallock, and Holland, *ibid.*, p. 1241) have recently described the use of diphenyl ether and the eutectic of diphenyl and diphenyl ether (Dowtherm A) for this purpose, the latter having the advantage of being liquid at room temperature. Other high boiling inert solvents should be equally suitable, quinoline, for example, having been applied for this purpose (Dr. F. H. S. Curd, private communication).

With *o*- and *p*-substituted amines the constitutions of the products formed in the Conrad–Limpach reaction are unequivocal. With *m*-substituted amines, however, two products may be obtained since ring-closure may take place at either the 2- or the 6-position of the arylamino-group; both were isolated in the ring-closures of ethyl 2-*m*-anisidino*cyclo*hex-1-enecarboxylate, which yielded 8- (VI) and 6-*methoxy*-1 : 2 : 3 : 4-*tetrahydroacridone* (VII), and ethyl β-*m*-anisidino-α-*n*-heptylcrotonate, which yielded endochin (I), m. p. 213—214°, and the isomeric 4-*hydroxy*-5-*methoxy*-3-n-*heptylquinaldine* (VIII), m. p. 219—220°. Leonard, Herbrandson, and Van Heyningen (*J. Amer. Chem. Soc.*, 1946, **68**, 1279) have recently studied the latter ring-closure but do not record the isolation of (VIII) and claim, on the basis of analytical data, to have isolated the demethylated substance, 4 : 5-dihydroxy-3-*n*-heptylquinaldine, m. p. 218—218·5° (corr.), in addition to (I), m. p. 218·5—219·5° (corr.). In both these cases ring-closure at the position para to the methoxyl group greatly preponderated, in contrast with the purely aromatic series where approximately equal proportions of 2- and 4-methoxyacridones are formed in the ring-closure of *N*-*m*-anisylanthranilic acid (Lehmstedt and Schrader, *Ber.*, 1937, **70**, 838). An authentic specimen of (VI) was obtained by applying the Niementowski–Borsche–Tiedtke reaction to 4-methoxyanthranilic acid and *cyclo*hexanone, but the yield was poor because of the ease with which this particular anthranilic acid undergoes decarboxylation. The melting points of 7-methoxy- (V) and 7-ethoxy-1 : 2 : 3 : 4-tetrahydroacridone (X) recorded here differ from those recorded in the literature (see pp. 1036, 1037), but we have carefully repeated these preparations and have fully confirmed our own observations.

Tests for causal prophylactic activity in *P. gallinaceum* infections in 10-day old chicks were carried out using the technique previously outlined (Fuller, Tonkin, and Walker, *loc. cit.*; King and Tonkin, *loc. cit.*) and the results are recorded in the Table. The minimal effective doses are those, given orally twice daily for the first four days and commencing two hours before infection, which gave definite indications of activity in comparison with untreated controls. In some cases no parasites were observed in the blood during the period of observation; sub-inoculations into clean chicks from such birds were carried out in a few cases and, if no infection resulted in the recipients, the donors were considered as having been sterilized of their infections (S). Where no sub-inoculations were carried out the result is recorded as presumably sterilized (? S). These observations (S and ? S) were, of course, made on higher dosages than those recorded as minimal. In a number of cases tests for therapeutic activity were carried out and the results are recorded in the Table; + denotes definite action, +— slight action, and — no action. The following substances, prepared by known methods, were also examined for prophylactic action and found to be inactive: 2 : 4-dihydroxyquinoline, 4-hydroxyquinaldine, 4-hydroxy-6-methoxyquinaldine, 4-hydroxy-8-methoxyquinaldine, 2-hydroxy-6-methoxy-lepidine, 1 : 2 : 3 : 4-tetrahydroacridone, and 3-methoxyacridone. From an inspection of the

Table and the preceding list, it is obvious that activity was only to be found in substances conforming to type (IV), as mentioned above. The necessity for the presence of a substituent in the benzene ring is clearly indicated by the inactivity of the simple 1 : 2 : 3 : 4-tetrahydroacridone and, of the substituents examined, methoxyl was more favourable than chloro-, which was more favourable than the ethoxyl group as indicated by the order of activities, (V) > (XI) > (X), and (XXIV) = (XXVI) > (XXV). The effect of the position of the methoxyl group in the benzene ring was marked, the position corresponding to the 7-position of quinoline being as a rule favourable as indicated by endochin (I), in which R′ and R″ of (IV) are of unequal size, but where R′ and R″ are of equal size as in (V), (VI), and (IX) the position corresponding to the 6-position of quinoline appeared to be most favourable, and weighting the alicyclic ring had a dystherapeutic effect.

Experimental.

General Method for the Synthesis of 1 : 2 : 3 : 4-*Tetrahydroacridones,* 12-*Hydroxy*-2 : 3-*dihydro*-β-*quinindenes, and* 4-*Hydroxyquinolines.*—Equimolecular amounts, usually 0·1 g.-mol., of the appropriate aromatic primary amine and β-keto-ester were mixed—with warming, if necessary, in the case of solid amines—and the mixture, treated with one drop of concentrated hydrochloric acid (Coffey, Thomson, and Wilson, *J.*, 1936, 856), was set aside in a partly evacuated desiccator for several days at 37°. The crude β-arylamino-$\Delta^{\alpha\beta}$-unsaturated esters were cyclized by being added slowly to a weight of boiling diphenyl four times that of the combined starting materials. Evolution of alcohol took place readily and the boiling solutions were refluxed for 15 minutes after the end of the addition. On cooling, the products usually crystallised when the temperature fell to about 100°. When cold, the diphenyl was removed with ether, and the crude products, usually cream-coloured, were crystallised from suitable

Antimalarial Activity in P. gallinaceum *Infections.*

	Prophylactic Test.		Therapeutic Test.
Tetrahydroacridones:	Min. effective dose (mg./100 g. chick).	Remarks.	
(V) 7-Methoxy-	12·5	?S	+
(VI) 8-*Methoxy*-	25		+−
(IX) 9-Methoxy-	37·5		−
(X) 7-Ethoxy-	inactive		
(XI) 7-Chloro-	100	slight act.	−
(XII) 7-Methyl-	inactive *		
(XIII) 7 : 8-Dimethoxy-	inactive *		
(XIV) 7-Methoxy-3-methyl-	inactive *		
(XV) 8-*Methoxy*-3-*methyl*-	50	S	
(XVI) 9-*Methoxy*-3-*methyl*-	50		
(XVII) 7-*Methoxy*-1-*methyl*-	62·5	toxic	
(XVIII) 8-*Methoxy*-1-*methyl*-	*ca.* 25	S	
(XIX) 9-*Methoxy*-1-*methyl*-	50	toxic	
(XX) 7-*Methoxy*-3-*ethyl*-	inactive *		
(XXI) 8-*Methoxy*-3-*ethyl*-	100	?S	
(XXII) 9-*Methoxy*-3-*ethyl*-	inactive *		
(XXIII) 7-*Methoxy*-1-*ethyl*-	100	very slight	
Dihydro-β-quinindenes:			
(XXIV) 12-*Hydroxy*-9-*methoxy*-	37·5		+
(XXV) 12-*Hydroxy*-9-*ethoxy*-	inactive		
(XXVI) 12-*Hydroxy*-9-*chloro*-	31		+
4-Hydroxyquinaldines:			
(XXVII) 6-*Methoxy*-3-*ethyl*-	inactive	toxic	
(XXVIII) 6-*Methoxy*-3-n-*heptyl*-	inactive *		
(I) 7-Methoxy-3-*n*-heptyl-	50	S	+
(XXIX) 8-*Methoxy*-3-n-*heptyl*-	*ca.* 100		
Sulphadiazine	25		

* Highest dose tested: 100 mg.

solvents. Diphenyl was used in the same arbitrarily selected proportion throughout, but recent work (Price and Roberts, *loc. cit.*) indicates that there may be an optimal concentration for each particular ring-closure.

7-*Methoxy*-1 : 2 : 3 : 4-*tetrahydroacridone* (V).—Obtained in an overall yield of 86% from *p*-anisidine and ethyl *cyclo*hexanone-2-carboxylate, the compound crystallised from alcohol or, better, pyridine in flat rectangular plates, m. p. 313° (Found: C, 73·6; H, 6·6; N, 6·3. Calc. for $C_{14}H_{15}O_2N$: C, 73·4; H, 6·6; N, 6·1%). Basu and Das Gupta (*J. Indian Chem. Soc.*, 1937, **14**, 468) record m. p. 295°; Hughes and Lions (*J. Proc. Roy. Soc., New South Wales*, 1938, **71**, 458) record m. p. 284°; Bukhsh and Desai (*Proc. Indian Acad. Sci.*, 1939, *A*, **10**, 262) record m. p. 285—286°. The intermediate ethyl 2-*p*-anisidino-*cyclo*hex-1-enecarboxylate separated from methyl alcohol in prisms, m. p. 70° (Found: C, 69·7; H, 7·7;

N, 5·4. Calc. for $C_{16}H_{21}O_3N$: C, 69·9; H, 7·6; N, 5·1%). Hughes and Lions (*loc. cit.*) record m. p. 71°; Bukhsh and Desai (*loc. cit.*) record m. p. 71—72°.

8-*Methoxy*-1 : 2 : 3 : 4-*tetrahydroacridone* (VI).—(*a*) 4-Methoxyanthranilic acid (4 g.) (preparation below) and *cyclo*hexanone (4 g.) were mixed and heated to 220° fairly rapidly and the mixture was kept at 220—230° for an hour. The mixture was cooled and treated with ether to remove *m*-anisidine, arising from decarboxylation, and unreacted *cyclo*hexanone. The insoluble 8-*methoxytetrahydroacridone* (0·3 g.; 5%) separated from spirit in small hexagonal plates, m. p. 309° (Found: C, 73·0; H, 6·5; N, 6·3. $C_{14}H_{15}O_2N$ requires C, 73·4; H, 6·6; N, 6·1%). The *m*-anisidine, arising as a by-product, was characterised as the acetyl derivative, m. p. and mixed m. p. 80°.

(*b*) The crude cyclization product obtained in 72% yield from *m*-anisidine and ethyl *cyclo*hexanone-2-carboxylate was a mixture of the 8- and 6-methoxy-compounds which could not be separated satisfactorily by crystallisation. The mixture (17 g.) was therefore dissolved in twice its weight of warm glacial acetic acid and then treated with 1½ volumes of concentrated hydrochloric acid. The hydrochloride, which separated on cooling in the ice-chest, was collected and drained thoroughly. The base (10·7 g.), regenerated from the solid hydrochloride with aqueous ammonia, then separated from spirit in hexagonal plates, m. p. and mixed m. p. 309° (Found: C, 73·1; H, 6·5; N, 6·3%).

6-*Methoxy*-1 : 2 : 3 : 4-*tetrahydroacridone* (VII).—The acetic–hydrochloric acid mother liquors from the above experiment, on evaporation to dryness and treatment with aqueous ammonia, afforded the crude 6-*methoxy*-isomer (5·9 g.) which separated from spirit in flattened needles (1·4 g.), m. p. 326°, depressed to 284° on admixture with the 8-methoxy-compound formed in the same reaction (Found: C, 73·5; H, 6·5; N, 6·1. $C_{14}H_{15}O_2N$ requires C, 73·4; H, 6·6; N, 6·1%).

9-*Methoxy*-1 : 2 : 3 : 4-*tetrahydroacridone* (IX).—Obtained in 60% yield from *o*-anisidine and ethyl *cyclo*hexanone-2-carboxylate, the compound separated from *n*-butyl alcohol in plates, m. p. 286—288° (Found: C, 73·5; H, 6·6; N, 6·4. Calc. for $C_{14}H_{15}O_2N$: C, 73·4; H, 6·6; N, 6·1%). Hughes and Lions (*loc. cit.*) record m. p. 278°; Bukhsh and Desai (*loc. cit.*) record m. p. 277—279°.

7-*Ethoxy*-1 : 2 : 3 : 4-*tetrahydroacridone* (X).—Obtained in 87% yield from *p*-phenetidine and ethyl *cyclo*hexanone-2-carboxylate, the compound separated from pyridine in needles or from alcohol in prisms, m. p. 292—293° (Found: C, 74·1; H, 7·1; N, 5·8. Calc. for $C_{15}H_{17}O_2N$: C, 74·1; H, 7·0; N, 5·8%). Hughes and Lions (*loc. cit.*) record m. p. > 300°; Bukhsh and Desai (*loc. cit.*) record m. p. >350°. The intermediate ethyl 2-*p*-phenetidino*cyclo*hex-1-enecarboxylate separated from alcohol in long prisms, m. p. 87° (Found: C, 70·0; H, 8·0; N, 4·9. Calc. for $C_{17}H_{23}O_3N$: C, 70·6; H, 8·0; N, 4·9%). Hughes and Lions (*loc. cit.*) record m. p. 87°; Bukhsh and Desai (*loc. cit.*) record m. p. 88°.

7-*Chloro*-1 : 2 : 3 : 4-*tetrahydroacridone* (XI).—Obtained in 74% yield from *p*-chloroaniline and ethyl *cyclo*hexanone-2-carboxylate, the compound crystallised from alcohol in microscopic prisms, m. p. > 330° (Found: C, 67·0; H, 5·3; N, 6·2. Calc. for $C_{13}H_{12}ONCl$: C, 66·9; H, 5·1; N, 6·0%). Basu and Das Gupta (*loc. cit.*) record m. p. 380°. The intermediate ethyl 2-*p*-chloroanilino*cyclo*hex-1-enecarboxylate separated from aqueous alcohol in short prisms, m. p. 67°, whereas Basu and Das Gupta (*loc. cit.*) record m. p. 90° (Found: C, 64·7; H, 6·7; N, 5·2. Calc. for $C_{15}H_{18}O_2NCl$: C, 64·4; H, 6·4; N, 5·0%).

7-*Methyl*-1 : 2 : 3 : 4-*tetrahydroacridone* (XII).—Obtained in 40% yield from *p*-toluidine and ethyl *cyclo*hexanone-2-carboxylate, the compound separated from aqueous acetic acid in thin laths, m. p. > 330° (Found: C, 78·9; H, 7·1; N, 6·8. Calc. for $C_{14}H_{13}ON$: C, 78·9; H, 7·0; N, 6·6%). Sen and Basu (*J. Indian Chem. Soc.*, 1930, **7**, 435) record m. p. 340°; Reed (*J.*, 1944, 425) records m. p. 374°.

7 : 8-*Dimethoxy*-1 : 2 : 3 : 4-*tetrahydroacridone* (XIII).—Obtained in 65% yield from 4-aminoveratrole and ethyl *cyclo*hexanone-2-carboxylate, the compound separated from aqueous alcohol in microscopic plates, m. p. > 330° (Found: C, 69·9; H, 6·6; N, 5·6. Calc. for $C_{15}H_{17}O_3N$: C, 69·5; H, 6·6; N, 5·4%). Lions (*ibid.*, p. 242) records m. p. > 300°.

12-*Hydroxy*-9-*methoxy*-2 : 3-*dihydro*-β-*quinindene* (XXIV).—Obtained in 59% yield from *p*-anisidine and ethyl *cyclo*pentanone-2-carboxylate, the *compound* separated from alcohol in fine needles, m. p. > 330° with prior darkening (Found: C, 72·7; H, 6·3; N, 6·7. $C_{13}H_{13}O_2N$ requires C, 72·6; H, 6·1; N, 6·5%). The intermediate *ethyl* 2-p-*anisidino*cyclo*pent*-1-*enecarboxylate* separated from aqueous alcohol in short needles, m. p. 54—55° (Found: C, 69·0; H, 7·3. $C_{15}H_{19}O_3N$ requires C, 68·9; H, 7·3%).

12-*Hydroxy*-9-*ethoxy*-2 : 3-*dihydro*-β-*quinindene* (XXV).—Obtained in 59% yield from *p*-phenetidine and ethyl *cyclo*pentanone-2-carboxylate, the *compound* crystallised from alcohol in aggregates of irregular plates, m. p. approx. 300° with previous darkening (Found: C, 73·4; H, 6·1; N, 6·2. $C_{14}H_{15}O_3N$ requires C, 73·4; H, 6·6; N, 6·1%). The intermediate *ethyl* 2-p-*phenetidino*cyclo*pent*-1-*enecarboxylate* separated from spirit in short prisms, m. p. 53° (Found: C, 70·0; H, 7·7; N, 5·1. $C_{14}H_{21}O_3N$ requires C, 69·9; H, 7·6; N, 5·1%).

9-*Chloro*-12-*hydroxy*-2 : 3-*dihydro*-β-*quinindene* (XXVI).—Obtained in 60% yield from *p*-chloroaniline and ethyl *cyclo*pentanone-2-carboxylate, the *compound* crystallised from aqueous acetic acid in long needles, m. p. approx. 330° with prior darkening (Found: C, 65·8; H, 4·5; N, 6·6. $C_{13}H_{10}ONCl$ requires C, 65·8; H, 4·6; N, 6·4%).

7-*Methoxy*-3-*methyl*-1 : 2 : 3 : 4-*tetrahydroacridone* (XIV).—Obtained in 40% yield from *p*-anisidine and ethyl 4-methyl*cyclo*hexanone-2-carboxylate, the compound separated from 50% alcohol or aqueous pyridine in microscopic rectangular plates, m. p. 346—347° (Found: C, 73·9; H, 7·1; N, 6·1. Calc. for $C_{15}H_{17}O_2N$: C, 74·1; H, 7·0; N, 5·8%). Basu and Das Gupta (*loc. cit.*) record m. p. 335°.

8-*Methoxy*-3-*methyl*-1 : 2 : 3 : 4-*tetrahydroacridone* (XV).—Presumably contaminated initially with the 6-methoxy-isomer in the reaction product obtained in 56% yield from *m*-anisidine and ethyl 4-methyl*cyclo*hexanone-2-carboxylate, the *compound* separated from pyridine in microscopic needles, m. p. 324° (Found: C, 74·2; H, 6·8; N, 6·1. $C_{15}H_{17}O_2N$ requires C, 74·1; H, 7·0; N, 5·8%).

9-*Methoxy*-3-*methyl*-1 : 2 : 3 : 4-*tetrahydroacridone* (XVI).—Obtained in 62% yield from *o*-anisidine and ethyl 4-methyl*cyclo*hexanone-2-carboxylate, the *compound* separated from alcohol in rectangular plates, m. p. 270—273° (Found: C, 73·7; H, 7·1; N, 6·1. $C_{15}H_{17}O_2N$ requires C, 74·1; H, 7·0; N, 5·8%).

7-*Methoxy*-1-*methyl*-1 : 2 : 3 : 4-*tetrahydroacridone* (XVII).—Obtained in 41% yield from *p*-anisidine and ethyl 6-methyl*cyclo*hexanone-2-carboxylate, the *compound* separated from aqueous alcohol in

rectangular plates, m. p. 280—281° (Found: C, 73·8; H, 7·0; N, 5·7. $C_{15}H_{17}O_2N$ requires C, 74·1; H, 7·0; N, 5·8%).

8-*Methoxy*-1-*methyl*-1 : 2 : 3 : 4-*tetrahydroacridone* (XVIII).—Obtained in 23% yield from *m*-anisidine and ethyl 6-methyl*cyclo*hexanone-2-carboxylate, the *compound* crystallised from spirit in fine needles, m. p. 277—278° (Found: C, 74·0; H, 7·2; N, 5·6. $C_{15}H_{17}O_2N$ requires C, 74·1; H, 7·0; N, 5·8%).

9-*Methoxy*-1-*methyl*-1 : 2 : 3 : 4-*tetrahydroacridone* (XIX).—Obtained in 24% yield from *o*-anisidine and ethyl 6-methyl*cyclo*hexanone-2-carboxylate, the *compound* separated from ethyl acetate in small cubes, m. p. 245—246° (Found: C, 74·0; H, 7·4; N, 5·9. $C_{15}H_{17}O_2N$ requires C, 74·1; H, 7·0; N, 5·8%).

7-*Methoxy*-3-*ethyl*-1 : 2 : 3 : 4-*tetrahydroacridone* (XX).—Obtained in 72% yield from *p*-anisidine and ethyl 4-ethyl*cyclo*hexanone-2-carboxylate, the *compound* separated from alcohol in rectangular plates, m. p. 334° (Found: C, 74·9; H, 7·1; N, 5·7. $C_{16}H_{19}O_2N$ requires C, 74·7; H, 7·4; N, 5·4%).

8-*Methoxy*-3-*ethyl*-1 : 2 : 3 : 4-*tetrahydroacridone* (XXI).—Obtained in 64% yield from *m*-anisidine and ethyl 4-ethyl*cyclo*hexanone-2-carboxylate, the *compound* was purified with some difficulty from the 6-methoxy-isomer, formed simultaneously, by crystallisation from methyl alcohol and separated in fine flattened needles, m. p. 291° (Found: C, 74·8; H, 7·4; N, 5·6. $C_{16}H_{19}O_2N$ requires C, 74·7; H, 7·4; N, 5·4%). A pure specimen of the 6-methoxy-isomer was not isolated.

9-*Methoxy*-3-*ethyl*-1 : 2 : 3 : 4-*tetrahydroacridone* (XXII).—Obtained in 64% yield from *o*-anisidine and ethyl 4-ethyl*cyclo*hexanone-2-carboxylate, the *compound* separated from spirit in microscopic prisms, m. p. 218—219° (Found: C, 74·6; H, 7·2; N, 5·6. $C_{16}H_{19}O_2N$ requires C, 74·7; H, 7·4; N, 5·4%). The intermediate *ethyl* 2-*o*-*anisidino*-5-*ethyl*cyclo*hex*-1-*enecarboxylate* separated from methyl alcohol in rectangular plates, m. p. 60° (Found: C, 70·8; H, 8·5; N, 4·9. $C_{18}H_{25}O_2N$ requires C, 71·3; H, 8·3; N, 4·6%).

7-*Methoxy*-1-*ethyl*-1 : 2 : 3 : 4-*tetrahydroacridone* (XXIII).—Obtained in 40% yield from *p*-anisidine and ethyl 6-ethyl*cyclo*hexanone-2-carboxylate, the *compound* separated from methyl alcohol in rectangular plates, m. p. 252—253° (Found: C, 74·9; H, 7·7; N, 5·8. $C_{16}H_{19}O_2N$ requires C, 74·7; H, 7·4; N, 5·4%).

4-*Hydroxy*-6-*methoxy*-3-*ethylquinaldine* (XXVII).—Obtained in 46% yield from *p*-anisidine and ethyl α-ethylacetoacetate, the *compound* separated from pyridine in fine needles, m. p. 290° (Found: C, 72·0; H, 7·0; N, 6·6. $C_{12}H_{15}O_2N$ requires C, 72·0; H, 7·0; N, 6·5%).

4-*Hydroxy*-6-*methoxy*-3-n-*heptylquinaldine* (XXVIII).—Obtained in 77% yield from *p*-anisidine and ethyl α-*n*-heptylacetoacetate, the *compound* separated from methyl alcohol in fine rectangular plates, m. p. 236—237° (Found: C, 75·6; H, 8·9; N, 5·0. $C_{18}H_{25}O_2N$ requires C, 75·3; H, 8·7; N, 4·9%).

4-*Hydroxy*-7-*methoxy*-3-n-*heptylquinaldine* (*Endochin*) (I) *and* 4-*Hydroxy*-5-*methoxy*-3-n-*heptylquinaldine* (VIII).—A mixture of isomers was obtained in 61% yield from *m*-anisidine and ethyl α-*n*-heptylacetoacetate, which were allowed to interact in the first stage for 7 days at 37°. Crystallisation from methyl alcohol readily afforded the bulk (*ca.* 2/3) of the product, consisting of (I), which separated in fine flattened needles, m. p. 213—214° (Found: C, 75·7; H, 8·5; N, 5·2. Calc. for $C_{18}H_{25}O_2N$: C, 75·3; H, 8·7; N, 4·9%). *Combined Intelligence Objectives Sub-Committee*, 1945, Item No. 24, File No. XXV—54 (p. 38) records m. p. 207—212°; Leonard *et al.* (*loc. cit.*) record m. p. 218·5—219·5° (corr.).

The mother liquors on concentration to small bulk afforded an obvious mixture (7·9 g.), m. p. 180—185°. This mixture on treatment with N-hydrochloric acid (100 c.c.) gave a sticky gum which slowly hardened. The solid was collected and the acid filtrate yielded only traces of material (< 0·1 g.) on treatment with excess of ammonia. The solid dissolved readily in methyl alcohol and the clear solution was evaporated to a syrupy consistency. On addition of water (*ca.* 40 c.c.) a sticky gum reappeared, giving way, on addition of methyl alcohol (*ca.* 20 c.c.), to fine needles. These were collected, the mother liquors being retained (see below), and, on treatment in methyl alcoholic solution with aqueous ammonia, afforded a further amount (4·4 g.) of (I), m. p. and mixed m. p. 213—214°. The aqueous methyl alcohol mother liquors, on treatment with aqueous ammonia, afforded (VIII) (2·95 g.), m. p. 213°, depressed to 173—193° on admixture with (I). The pure *compound* separated from a small volume of methyl alcohol, or from a larger volume of 50% ethyl alcohol, in clusters of fine needles, m. p. 219—220° (Found: C, 75·4; H, 8·5; N, 4·7; OMe, 10·2. $C_{18}H_{25}O_2N$ requires C, 75·3; H, 8·7; N, 4·9; OMe, 10·8%).

4-*Hydroxy*-8-*methoxy*-3-n-*heptylquinaldine* (XXIX).—Obtained in 60% yield from *o*-anisidine and ethyl α-*n*-heptylacetoacetate, the *compound* crystallised from methyl alcohol in fine prisms, m. p. 155—156° (Found: C, 75·1; H, 8·9; N, 5·1. $C_{18}H_{25}O_2N$ requires C, 75·3; H, 8·7; N, 4·9%).

2-*Nitro*-4-*methoxyphenyl Cyanide*.—3-Nitro-4-aminoanisole was submitted to the Sandmeyer reaction using a technique previously described (Fuller, Tonkin, and Walker, *loc. cit.*), affording a 75% yield of recrystallised material separating from methyl alcohol in small plates, m. p. 139° (Found: N, 15·7. Calc. for $C_8H_6O_3N_2$: N, 15·7%). Cook *et al.* (*J.*, 1945, 861), using cuprous cyanide, obtained a somewhat lower yield (crude) and record m. p. 140°.

2-*Nitro*-4-*methoxybenzoic Acid*.—The preceding cyanide (50 g.) was refluxed for 5 hours with a mixture of equal volumes of glacial acetic acid, concentrated sulphuric acid, and water (each 100 c.c.), crystals separating after about 1½ hours. The cooled mixture was treated with about 2 volumes of water and the product was collected and re-precipitated (45 g.) from solution in aqueous ammonia; m. p. 195—196° as recorded by Simonsen and Rau (*J.*, 1917, **111**, 235) and by Ashley, Perkin, and Robinson (*J.*, 1930, 393).

4-*Methoxyanthranilic Acid*.—The preceding nitro-acid (45 g.) was dissolved in a slight excess of 2N-ammonia and hydrogenated in the presence of palladised strontium carbonate (5 g.) at 45 atm. The calculated fall in pressure was observed in about 20 minutes and absorption of hydrogen then ceased. The filtered solution was acidified to about pH 4 and the product (35·4 g.) was collected; m. p. 180° (efferv.). On account of ready decarboxylation, recrystallisation from *ca.* 40% aqueous acetic acid was wasteful but afforded fine prisms, m. p. 180—181° (efferv.). Friedländer, Bruckner, and Deutsch (*Annalen*, 1912, **388**, 46) record m. p. 166° (decomp.); Ullmann and Dootson (*Ber.*, 1918, **51**, 20) record m. p. 172° (decomp.).

Ethyl α-n-*Heptylideneacetoacetate*.—A mixture of freshly distilled oenanthal (100 g.) and ethyl

acetoacetate (114 g.) was cooled in a freezing mixture and saturated with dry hydrogen chloride. After 18 hours in the ice-chest the mixture was poured into water and extracted with ether. The extract was washed well with water, dried, and fractionated, affording a colourless oil (158 g.), b. p. 150—152°/14 mm. (Found: C, 69·1; H, 10·0. Calc. for $C_{13}H_{22}O_3$: C, 69·0; H, 9·7%). Knoevenagel (*Ber.*, 1898, **31**, 737) used piperidine as catalyst and recorded b. p. 145°/10 mm.

Ethyl α-n-Heptylacetoacetate.—The preceding unsaturated ester (145 g.) was hydrogenated in ethyl alcohol (400 c.c.) with palladised strontium carbonate (7 g.) at 45 atm. The calculated fall in pressure was observed in about 20 minutes and no further absorption of hydrogen took place. The product, a colourless oil (133 g.), distilled at 144—146°/11 mm. (Found: C, 68·3; H, 10·5. Calc. for $C_{13}H_{24}O_3$: C, 68·4; H, 10·5%). Wojcik and Adkins (*J. Amer. Chem. Soc.*, 1934, **56**, 2424) record b. p. 130—132°/7 mm.

The authors are greatly indebted to Mr. L. V. Sharp for much preparative assistance and to Mrs. A. M. Yates, B.Sc., for assistance in carrying out antimalarial tests.

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193. *β-Phellandrene Tetrabromide.*

By P. A. Berry and A. Killen Macbeth.

The optically active tetrabromide isolated from the terpene fraction of *E. cneorifolia* oil is derived from *l*-β-phellandrene and is identical with samples prepared from *l*-β-phellandrene derived from Canada-balsam oil. *d*-β-Phellandrene from water-fennel oil also forms an optically active tetrabromide. The β-phellandrene tetrabromides are characterised by rotations of opposite sign to that of the hydrocarbon from which they are derived.

In a previous paper (Berry, Macbeth, and Swanson, *J.*, 1937, 1443) it was shown that a seasonal variation occurred in the oil of *Eucalyptus cneorifolia* with an increase in the terpene content from a minimum of some 10% to a maximum approaching 50% which is attained during the period of active growth in the early summer months. The presence of *l*-α- and *l*-β-phellandrene was established, and after further examination of the terpene fraction it was reported by Berry and Macbeth (*Nature*, 1945, **156**, 175) that a crystalline tetrabromide can be isolated after bromine vapour has been aspirated through solutions of such terpene fractions in acetic acid, and the reaction mixture stored for some days in the refrigerator. The crystalline tetrabromide is separated in amounts corresponding with upwards of 20% of the total terpene when the hydrocarbon is dissolved in about four times its weight of acetic acid, and excess of bromine introduced whilst the temperature is kept below 0°.

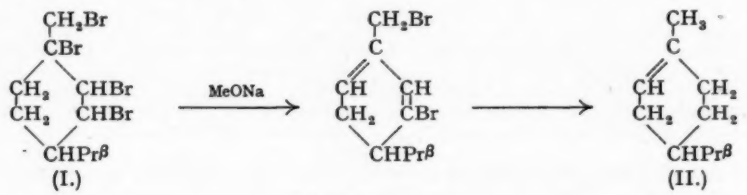
Analysis of the *tetrabromide* showed the formula to be $C_{10}H_{16}Br_4$, and in view of the fact that the substituent groups in the cyclic compounds occurring in *E. cneorifolia* oil are in the para-positions it may reasonably be concluded that the progenitor of the tetrabromide is a *p*-menthadiene. Of the fourteen possible structures seven inactive compounds are excluded as the tetrabromide is dextrorotatory, and of the remaining seven only two (limonene and *p*-mentha-2 : 8(9)-diene) are optically active and without conjugated double bonds. Henry and Paget (*J.*, 1925, **127**, 1649) isolated from oil of chenopodium an inactive tetrabromide which they considered was derived from *p*-mentha-2 : 8(9)-diene. We have confirmed this observation excepting that our tetrabromide had slight optical activity. The tetrabromides from limonene and dipentene have also been re-examined, and as their properties differ markedly from those of the tetrabromide from *E. cneorifolia* these substances must also be excluded. One is therefore forced to consider the para-menthadienes containing a conjugated system of double bonds despite the fact that crystalline tetrabromides derived from such substances are not described in the literature.

The tetrabromide now described is debrominated by magnesium in ether and yields a hydrocarbon, $C_{10}H_{16}$, which is readily converted into the tetrabromide again. This hydrocarbon showed the characteristics of *l*-β-phellandrene; in particular it formed a nitrosite the mutarotation of which was similar to that of the nitrosite derived from a sample of *l*-β-phellandrene from Canada-balsam oil. Authentic samples of *l*-β-phellandrene gave tetrabromides identical with that derived from the terpene fractions of *E. cneorifolia* oil, in particular having m. p. 118—119° after recrystallisation from ethyl acetate and a specific rotation of approximately +49° in the same solvent, the value being unchanged even after two months. The specific rotation in chloroform was higher (+53·6°) and these solutions too showed little change in rotation on storage.

The chief feature of the tetrabromide derived from β-phellandrene is the change of sign of

rotation, the lævorotatory hydrocarbon giving a dextrorotatory tetrabromide. This characteristic property provides a convenient and useful criterion for β-phellandrene, the identification of which has hitherto mainly rested on the optical properties of derivatives such as the nitrosite. A sample of *d*-β-phellandrene from water-fennel oil was available (Berry, Macbeth, and Swanson, *J.*, 1937, 1448), and this yielded a tetrabromide having m. p. 118—119° which had a specific rotation of the same magnitude as that derived from *l*-β-phellandrene but of opposite sign.

Wallach (*Annalen*, 1894, **281**, 129) examined the debromination of limonene tetrabromide by sodium methoxide and obtained as a product a monobromo-compound which nascent hydrogen converted into carveol methyl ether. The reaction with β-phellandrene tetrabromide (I) follows quite a different course, as only two bromine atoms are removed by the methoxide, and nascent hydrogen converts the product into a lævorotatory hydrocarbon of low density having the composition $C_{10}H_{18}$. The reactions appear to result in the formation of *l-p*-menth-1-ene (II), as the molecular refraction (45·85) agrees with the calculated value (45·7) and the compound forms a nitrosochloride having m. p. 93—94° and $[\alpha]_D$ −342° (ether). The nitrosochloride derived from *d-p*-menth-1-ene (Wallach, *Annalen*, 1911, **381**, 58; Vavon, *Compt. rend.*, 1911, **152**, 1675) has m. p. 95—96° and $[\alpha]_D$ +344°, the sign of rotation of the derivative being the same as that of the parent hydrocarbon.



(I.) (II.)

Experimental

Tetrabromide from Terpene Fraction of E. cneorifolia *Oil.*—Preliminary experiments showed that the amount of tetrabromide formed varied greatly with conditions, and the factors favourable to high yield were mainly (1) the use of freshly distilled terpene fraction dissolved in about four times its volume of acetic acid, (2) a bath temperature below 0° but not so low as to cause much crystallisation of acetic acid on the walls of the reaction vessel, (3) steady aspiration of bromine vapour at such a rate that bromination was completed within an hour and the additional excess of bromine introduced for a further fifteen minutes, (4) efficient stirring to ensure that the temperature of the reaction mixture did not rise above about 5°, and (5) subsequent storage in the refrigerator for several days.

In a typical experiment freshly distilled terpene (100 c.c.) having α_D −42·4° (homogeneous) was dissolved in acetic acid (350 c.c.) and brominated for 70 minutes, the flask being immersed in an ice–salt mixture. Bromine (140 g.) was rapidly absorbed during 45 minutes and aspiration was stopped after an excess (180 g. in all) had been introduced (70 minutes). The mixture was placed in the refrigerator, and crystallisation of the tetrabromide was beginning within an hour. After five days the crystals were removed at the pump and washed with cold acetic acid. Yield, 56 g. of crude tetrabromide having m. p. 109—110°, $[\alpha]_D$ 57·1° in chloroform (*c*, 4·468). This is equivalent to upwards of 20% of the terpene taken.

In another experiment terpene (100 c.c.; α_D −43·2°) in acetic acid (400 c.c.) was brominated by aspiration of bromine (195 g.) for an hour, the temperature of the bath being −8°. Some acetic acid crystallised on the walls during reaction and the yield of crude washed tetrabromide collected after seven days was 47 g. having m. p. 109—111, $[\alpha]_D$ 59·5°. In a further experiment terpene (75 c.c., α_D −38°) in acetic acid (300 c.c.) after treatment in a similar way with bromine (147 g.) gave crude washed tetrabromide (37·3 g.) having m. p. 108—110°, $[\alpha]_D$ 52·7° in chloroform. This corresponds with about 18% of terpene taken.

The combined yields of tetrabromide (140 g.) from the above preparations after four crystallisations from ethyl acetate gave pure tetrabromide as flat glistening plates having m. p. 116—117°, $[\alpha]_D$ 53·6° in chloroform (*c*, 5·41). Further recrystallisation raised the m. p. to 118—119°. The solubility in ethyl acetate at 17° is 10·4% w/w and tetrabromide of good quality can be recovered as a first crop after concentration of the mother liquors. The specific rotation of the *tetrabromide* in ethyl acetate is somewhat lower than in chloroform, a solution (*c*, 4·004) having a value of 48·8° which was unchanged after the solution had been kept for two months (Found: C, 26·4; H, 3·65; Br, 70·2. $C_{10}H_{16}Br_4$ requires C, 26·3; H, 3·5; Br, 70·1%).

Debromination of the Tetrabromide.—The method of debromination used was essentially that described by Brown and Lemke (*Ber.*, 1923, **56**, 1562) in the preparation of limonene from its tetrabromide by the action of magnesium in ether. Purified tetrabromide (39 g.) in anhydrous ether (196 c.c.) was gently warmed with magnesium (6·2 g.) and a trace of iodine. After 90 minutes the ethereal layer was separated and washed with water (twice), and the washings were used to wash the original lower (magnesium bromide) layer. The separated ether from this was washed with water and the total ether distilled to remove solvent and then steam distilled. From two such experiments unchanged tetrabromide (5·3 g.) was recovered from the steam-distillation flask, and an oil (15·8 g.) of low density (*d* 0·843) was recovered from the distillate. The hydrocarbon obtained on distilling the oil over sodium had $d_{15^\circ}^{15^\circ}$ 0·8411 and $[\alpha]_D^{20^\circ}$ −16·2°. It had the formula $C_{10}H_{18}$ and gave a nitrosite (Found: C, 88·3; H, 11·95. Calc.

C, 88·15; H, 11·8%). When brominated as described above the hydrocarbon gave a tetrabromide identical with the original.

Tetrabromide of l-β-Phelladrene.—The formation of a nitrosite suggested that the hydrocarbon was possibly a phellandrene, and this was supported by the fact that a terpene fraction from which the phellandrene was removed gave, on bromination, only a small quantity of crystals which were inactive and had m. p. 220°. This was evidently benzene hexabromide derived from traces of benzene in the solvents used during removal of the phellandrene as nitrosite. The bromination of *l*-β-phellandrene was therefore examined, the material being available as an old sample derived from Canada-balsam oil. On steam distillation this gave terpene having α_D −42°, and after bromination as described above crude tetrabromide (7·2 g.) was obtained in amount equivalent to about 10% of the terpene. It had m. p. 110—112°, $[\alpha]_D^{20°}$ 57·3° in ethyl acetate (*c*, 4·265), and after several recrystallisations from the same solvent the m. p. had risen to 116—117°. The sample showed no depression of m. p. on admixture with the pure tetrabromide derived from *E. cneorifolia* oil.

A small sample of the residue from water fennel oil from which *d*-cryptone and *d*-phellandral had been removed some years before was steam distilled, and the terpene collected (which contained *d*-β-phellandrene and was dextrorotatory) was brominated in the usual way. The crude tetrabromide of *d*-β-phellandrene had m. p. 111—113° and a high lævo-rotation ($[\alpha]_D$ −56·6°) in ethyl acetate (*c*, 5·492). After four recrystallisations from ethyl acetate the pure tetrabromide had m. p. 116—116·5°, and $[\alpha]_D^{20°}$ −55·1° in ethyl acetate (*c*. 4·046). The m. p. of the substance is the same as that of the tetrabromide of *l*-β-phellandrene and its optical activity of the same order, but of opposite sign.

The tetrabromide of *dl*-β-phellandrene was separated as long needles when a solution of equimolecular amounts of the *d*- and the *l*-compound in ethyl acetate was allowed to evaporate slowly. The substance was inactive and had m. p. 112—113°, not changed by further crystallisation.

Debromination by Sodium Methoxide.—The tetrabromide of *l*-β-phellandrene (50 g.) was refluxed for more than 8 hours with sodium methoxide (8 g. sodium in 100 c.c. of methyl alcohol). After the addition of some water the reaction mixture was steam distilled, and the oil (30 g.) recovered from the distillate was dried (KOH) and fractionated under reduced pressure. It distilled as a main fraction (28 g.) which was again refluxed for 7 hours with sodium methoxide, and the oil was worked up again giving a main fraction (26 g.) which distilled at 144—148°/11 mm. and had *d* 1·448; $[\alpha]_D$ 19·2°; $n_D^{18°}$ 1·5643. Bromine combined as sodium bromide in the still residue after the steam distillations amounted in the first case to 18·5 g. which is equivalent to the removal of 2·1 atoms of bromine from the tetrabromide. After the second treatment with methoxide bromine removed was assayed as equivalent to a further 0·2 atom only.

The partly debrominated oil (24 g.) was dissolved in absolute alcohol (250 c.c.) and gradually treated with sodium (20 g.), the mixture being heated on the water-bath as reaction slowed down. The oil collected on steam distillation still contained bromine and was again subjected to the action of nascent hydrogen. The oil then collected on steam distillation, after being dried (KOH), distilled at 75—76°/34 mm. and had $d_{15·5°}^{21°}$ 0·8228; $[\alpha]_D$ −81·2° (homogeneous); $n_D^{21°}$ 1·4581 (Found: C, 87·2; H, 13·0. Calc. for $C_{10}H_{18}$: C, 86·85; H, 13·1%). The oil readily decolorised bromine in acetic acid and gave a nitrosochloride, m. p. 93—94°, which was very stable and did not decompose on heating to 140°. In ether (*c*, 0·714) the nitrosochloride had $[\alpha]_D$ −342° which had fallen after 13 hours to −322° and after 85 hours to −280°. It appears that the compound is *l*-*p*-menth-1-ene as the constants are in good agreement with those recorded for *d*-*p*-menth-1-ene, the optical values being of opposite sign.

Other Tetrabromides.—In the course of the work several tetrabromides were prepared for comparison with the product obtained from *E. cneorifolia* oil. *d*-Limonene tetrabromide was prepared from sweet orange oil of pharmaceutical quality, and had m. p. 104—105°, $[\alpha]_D$ 79·2° in chloroform. Dipentene tetrabromide was prepared from a sample of dipentene kindly supplied by Professor T. G. Jones, and a further preparation was carried out from cineol. The tetrabromide was inactive and had m. p. 126—127°. A tetrabromide was also prepared from an imported sample of pharmaceutical oil of chenopodium; it had m. p. 115—116°, $[\alpha]_D$ 2·2° in chloroform (*c*, 16·13) (compare Henry and Paget, *loc. cit.*).

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194. *Molecular Rearrangement and Displacement of Arylamine Residues in α-Arylamino-ketones. Part I.*

By R. M. COWPER and T. S. STEVENS.

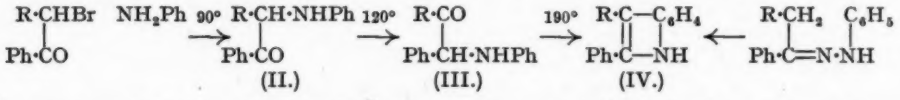
When an arylaminodeoxybenzoin (*e.g.*, II) is heated with a mixture of an arylamine and its hydrobromide, rearrangement may take place (to III); if the arylamine does not correspond to the arylamine residue in the ketone, this residue may be displaced by that of the reagent, with or without simultaneous rearrangement. The observations are only partly explicable by the mechanism proposed by Bischler for the rearrangements and displacements involved in the conversion of phenacylarylamines into arylindoles, and other mechanisms are discussed.

McGEOCH and STEVENS (*J.*, 1935, 1032) observed that the action of aniline on phenyl 1-bromo-2-phenylethyl ketone afforded an anomalous by-product (I):

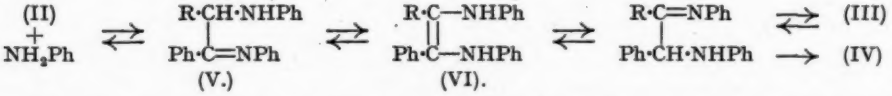
$$CH_2Ph{\cdot}CHBr{\cdot}COPh \longrightarrow CH_2Ph{\cdot}CH(NHPh){\cdot}COPh + CH_2Ph{\cdot}CO{\cdot}CHPh{\cdot}NHPh \quad (I.)$$

Related reactions of more tractable materials have been studied in detail, and the observations and tentative conclusions are reported now in view of publications by other workers in the same field (Crowther, Mann, and Purdie, *J.*, **1943**, **58**; Verkade and Janetzky, *Rec. Trav. chim.*, **1943**, **62**, 763, 775; Julian, Meyer, Magnani, and Cole, *J. Amer. Chem. Soc.*, **1945**, **67**, 1203). The results of the principal series of experiments are summarised in the table.

The α-bromo-derivatives of 4- and 4'-methoxydeoxybenzoin react in the first instance *normally*, by direct displacement, with aniline, *p*-toluidine, or methylaniline (Cowper and Stevens, *J.*, **1940**, **347**; which see for proofs of constitution of substances described in this paper); but at higher temperatures, in presence of arylamine and arylamine hydrobromide, such transformations as the following may occur (R = *p*-anisyl, throughout):



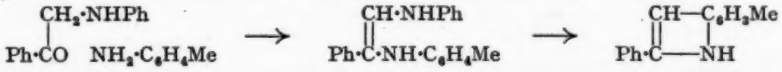
The conversion of the base (II) into (III) is sensibly complete, like the thermal transformation (Julian and Passler, *J. Amer. Chem. Soc.*, **1932**, **54**, 4756; cf. Luis, *J.*, **1932**, 2547) of the corresponding benzoin into its isomeride, R·CH(OH)·COPh ⟶ R·CO·CH(OH)Ph. It is plausibly explained on the basis of Bischler's mechanism for the formation of 2-phenylindole from anilinoacetophenone (*Ber.*, **1892**, **25**, 2860; **1893**, **26**, 1336; cf. Strain, *J. Amer. Chem. Soc.*, **1929**, **51**, 270):



This explanation does not exclude rearrangement of the *N*-methyl derivative of (II) in presence of methylaniline and its hydrobromide, through direct formation and hydrolysis of the intermediate (as VI); but the process might be expected to be more difficult, in view of the failure of the carbonyl group of benzoins to react with a secondary base (Cowper and Stevens, *loc. cit.*). In fact, no reaction was observed below 170°, higher temperatures leading, not to the methyl derivative of (III), but by indolisation to that of (IV). Indolisation is structurally excluded in *phenyl* α-(*N-methylmesidino*)-p-*methoxybenzyl ketone*, Ph·CO·CHR·NMe·$C_6H_2Me_3$, but when this was heated with methylmesidine and its hydrobromide at 170° it was recovered unchanged, and at 190° the only isolable product was nitrogen-free.

Julian *et al.* (*loc. cit.*) record similar (reversible) rearrangements, *i.e.*, (II; R = Me or CH_2Ph) ⟶ (III; R = Me or CH_2Ph), and also demonstrate the formation, under similar experimental conditions, of anilinodeoxybenzoin anil (as V) from anilinodeoxybenzoin and aniline.

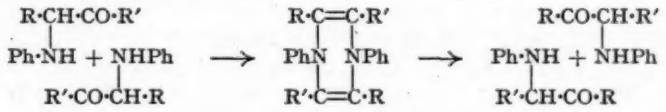
The Bischler mechanism accounts well for the conversion of anilinoacetophenone, by heating with excess of *p*-toluidine and its hydrochloride, into 2-phenyl-5-methylindole, aniline being in effect displaced by toluidine (Bischler, *loc. cit.* For other examples, see Julian *et al.*, *J. Amer. Chem. Soc.*, **1933**, **55**, 2105; **1945**, **67**, 1203; Verkade and Janetzky, *loc. cit.*):



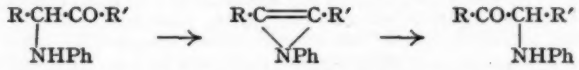
Such a displacement is not necessarily associated with indolisation; thus when (II) or (III) is heated at 120° with excess of *p*-toluidine and *p*-toluidine hydrobromide the product is the toluidino-analogue of (III), displacement being accompanied in the former case by rearrangement. Further similar results are recorded in the table.

The reactions of rearrangement and/or displacement so far discussed can be accommodated by the Bischler–Strain scheme; alternatively, a somewhat similar mechanism could be envisaged, involving as an intermediate stage a product of the type $(NHAr·CR{:}CPh)_2NAr$, discovered by Crowther, Mann, and Purdie (*loc. cit.*); but it is not clear why the *N*-methyl derivatives of (II) and (III) are unaffected by aniline–aniline hydrobromide up to 170°; and most surprising that (II), with methylaniline and its hydrobromide, readily affords (III) by rearrangement *without displacement*. The rearrangement of (II) is, moreover, smoothly effected by boiling with pyridine hydrobromide in pyridine or in butyl alcohol, a result explicable on Bischler's hypothesis only if part of the initial material furnishes free aniline by decomposition. This remote possibility was examined, and the strictly *intramolecular* character of the rearrangement

indicated, by heating a mixture of two arylamino-ketones with pyridine hydrobromide in pyridine and seeking evidence for an exchange of arylamine residues. For experimental convenience, one selected initial substance was desylanthranilic acid, $Ph{\cdot}CO{\cdot}CHPh{\cdot}NH{\cdot}C_6H_4{\cdot}CO_2H$, rearrangement of which is concealed by symmetry but from which aniline readily displaces anthranilic acid. The second initial material was (II), and the only products, isolated in good yield, were (III) and desylanthranilic acid. The result also discredits such a mechanism as the following (cf. Gabriel, *Ber.*, 1908, **41**, 1146) :



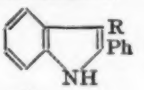
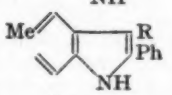
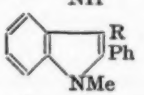
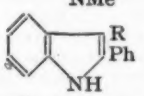
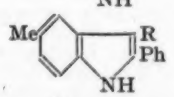
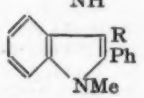
A strictly intramolecular rearrangement can be formulated in conventional structural terms only by postulating an intermediate having a three-membered ring :



For unsaturated C_2N rings compare Neber and Burgard (*Annalen*, 1932, **493**, 281).

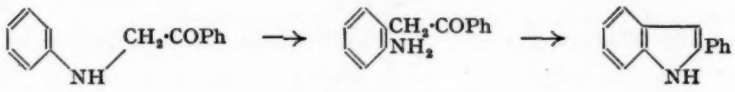
Attempts were also made to effect the *displacement* of one arylamine by another, where the Bischler mechanism could be excluded. When *α-anilinophenylacet-p-chloroanilide*, $NHPh{\cdot}CHPh{\cdot}CO{\cdot}NH{\cdot}C_6H_4Cl$, is heated at 200° with *p*-toluidine hydrobromide in *p*-toluidine, the aniline residue only is displaced; here the Bischler intermediate would be a tautomeric amidine, $NHPh{\cdot}CHPh{\cdot}C(:NPh){\cdot}NH{\cdot}C_6H_4Cl \rightleftharpoons NHPh{\cdot}CHPh{\cdot}C(NHPh):N{\cdot}C_6H_4Cl$, and its formation and decomposition would lead to extensive displacement of chloroaniline also. The high temperature necessary for the reaction, however, forbids the inference that a direct displacement is likely with arylamino-ketones at 120°. Under the same energetic conditions *p*-toluidine displaces aniline from benzylaniline; but benzhydryl-*p*-toluidine, which might have been expected to be very reactive, was unaffected by aniline–aniline hydrobromide at 150°.

It would appear, in sum, that in presence of a base and its salt an arylamino-ketone can react in two independent ways : (*a*) according to the Bischler–Strain scheme made very probable by Julian and his co-workers, leading in appropriate cases to arylamine displacement, to indolisation, and possibly to rearrangement; and (*b*) a strictly intramolecular rearrangement, perhaps by the mechanism suggested above.

Initial material.	Action of base + salt at 120° : NH_2Ph.	$NH_2{\cdot}C_7H_7$.	NHPhMe.	Product of indolisation.
R·CH(NHPh)·COPh	Rearr.	Rearr. + Displ.	Rearr.	
R·CH(NH·C₇H₇)·COPh	Rearr. + Displ.	Rearr.	Rearr.	
R·CH(NMePh)·COPh	Unch.	Unch.	Unch.	
R·CO·CH(NHPh)Ph	Unch.	Displ.		
R·CO·CH(NH·C₇H₇)Ph	Displ.	Unch.		
R·CO·CH(NMePh)Ph	Unch.	Unch.	Unch.	

Indolisation.—The base (II) and its analogues, each heated at 190—200° with the corresponding arylamine and its hydrobromide, yielded indoles; in all cases the product was that which would have resulted from the direct dehydration of an arylaminobenzyl *p*-anisyl ketone (as

III), the stable type when simple rearrangement can be effected. Attempted indolisation of (II) and of its *p*-toluidino-analogue in pyridine–pyridine hydrobromide gave as sole definable product a trace of nitrogen-free material, different in the two cases. This failure is not general (see Crowther, Mann, and Purdie, *loc. cit.*), and so not clearly significant as to the mechanism of Bischler synthesis. This investigation as a whole, however, shows that many of the anomalies recorded in this synthesis may be due to demonstrable transformations of the arylamino-ketones before cyclisation, and not to an *ortho*-migration as postulated by Crowther, Mann, and Purdie :



Experimental.

Rearrangement.—The following experiment is typical. Phenyl α-anilino-*p*-methoxybenzyl ketone (II) was heated with aniline (3 mols.) and aniline hydrobromide (0·5 mol.) at 115—120° for 3 hours. The mixture was treated with dilute hydrochloric acid and ether; the combined acid layers deposited long needles of the hydrochloride of (III), which with alcoholic ammonia gave the free base (85%), identified by mixed m. p. and by reduction to *p*-methoxyphenyl benzyl ketone. No unchanged (II) could be recovered.

The same result followed when (II) was boiled for 3 hours with pyridine hydrobromide in pyridine, or with pyridine hydrobromide or sulphate in *n*-butyl alcohol. It was recovered unchanged after 2·5 hours' heating with *p*-toluidine alone at 130°.

Phenyl N-*methylmesidino*-p-*methoxybenzyl ketone*, prepared from the related bromo-ketone and methylmesidine (Ullmann, *Annalen*, 1903, **327**, 110) in the usual way (Cowper and Stevens, *loc. cit.*), crystallised from alcohol in colourless needles, m. p. 89—90° (Found : N, 4·0. $C_{25}H_{27}O_2N$ requires N, 3·8%). It was unchanged after 5—6 hours' heating with methylmesidine and its hydrobromide at 170°; after 6 hours at 190° the only isolable product was a little nitrogen-free material, white, glittering laminæ from alcohol, m. p. 96—98°.

Displacement.—Phenyl α-anilino-*p*-methoxybenzyl ketone (II) or *p*-methoxyphenyl α-anilinobenzyl ketone (III) was heated at 115—120° for 3 hours with *p*-toluidine (3 mols.) and *p*-toluidine hydrobromide (0·5 mol.). Fractional crystallisation of the product from alcohol yielded in each case 75% of *p*-methoxyphenyl α-*p*-toluidinobenzyl ketone, m. p. and mixed m. p. 141—142°, and 25% of material, m. p. 115—117°, indistinguishable from a mixture of the toluidino-ketone with an equal quantity of (III).

Simultaneous Rearrangement of (II) *and Desylanthranilic Acid.*—The acid, from benzoin and anthranilic acid (Weckowicz, *Ber.*, 1908, **41**, 4144), crystallised from alcohol in cream-coloured plates, m. p. 225—227° (Found : N, 4·4. Calc. for $C_{21}H_{17}O_3N$: N, 4·2%). Heated with aniline and aniline hydrobromide, it rapidly yielded desylaniline with some unchanged material. Equal weights of desylanthranilic acid and the ketone (II) were boiled for 3 hours in pyridine with pyridine hydrobromide. After addition of ether the filtered solution was extracted successively with sodium hydroxide solution and hydrochloric acid. The extracts yielded respectively desylanthranilic acid and the ketone (III), each in 90% yield, with no evidence of any other product. Three parts of (II) to one of desylanthranilic acid were used in another experiment with similar results. For comparison, *phenyl* α-(*o-carboxyanilino*)-p-*methoxybenzyl ketone*, $MeO{\cdot}C_6H_4{\cdot}CHBz{\cdot}NH{\cdot}C_6H_4{\cdot}CO_2H$, was prepared from benzanisoin and anthranilic acid: white needles, m. p. 198—199° (Found : N, 4·0. $C_{22}H_{19}O_4N$ requires N, 3·9%). With aniline and aniline hydrobromide it yielded (III).

"Direct" Displacement of Arylamine Residues.—Ethyl α-anilinophenylacetate (Stöckenius, *Jahresber.*, 1878, 780) was unaffected by boiling *p*-chloroaniline, but when *p*-chloroaniline and the ester were added successively to ethylmagnesium bromide in ether at room temperature (compare Hardy, *J.*, 1936, 398), α-*anilinophenylacet*-p-*chloroanilide* was obtained : long prisms from alcohol, m. p. 157—158° (Found : N, 8·6; Cl, 10·4. $C_{20}H_{17}ON_2Cl$ requires N, 8·3; Cl, 10·5%). The anilide was boiled for 3 hours with *p*-toluidine hydrobromide (0·5 mol.) in *p*-toluidine (3 mols.), and the mixture treated with ether and dilute hydrochloric acid. The tarry mass deposited by the acid layer afforded, after several crystallisations from ammoniacal alcohol, white needles, m. p. 183—185°. These were identical with α-p-*toluidinophenylacet*-p-*chloroanilide*, prepared in the same way as the anilino-compound (Found : N, 7·9. $C_{21}H_{19}ON_2Cl$ requires N, 8·0%). When methylaniline was used in place of *p*-toluidine, much non-basic material was formed and no individual product could be isolated.

Benzylaniline hydrobromide was boiled under reflux with *p*-toluidine (5 mols.) for 4 hours, and the basified mixture distilled in steam. The non-volatile material, with benzenesulphonyl chloride in pyridine, gave benzenesulphonbenzyl-*p*-toluidide (mixed m. p.) which depressed the m. p. of benzenesulphonbenzylanilide. Benzhydryl-*p*-toluidine (Busch and Rinck, *Ber.*, 1905, **38**, 1768) was unchanged by 3 hours' heating with aniline and aniline hydrobromide at 150°; treatment at 180—190° afforded an oil, b. p. 239—245°/15 mm., which gave no crystalline derivative.

Indolisation.—The ketone (II) was heated at 200° for 2·5 hours with aniline (3 mols.) and aniline hydrobromide (0·5 mol.), and the crude non-basic material distilled in a vacuum and crystallised from alcohol. 2-*Phenyl*-3-p-*methoxyphenylindole* (IV) formed colourless prisms, m. p. 188—190° (Found : N, 4·5. $C_{21}H_{17}ON$ requires N, 4·7%). The same product was obtained in small yield by heating (II) with pyridine hydrobromide (0·1 mol.) at 180° for 30 mins.; and was also synthesised by boiling with alcoholic hydrochloric acid *phenyl* p-*methoxybenzyl ketone phenylhydrazone*, prepared in alcohol–acetic acid as cream-coloured plates, m. p. 124—125° (Found : N, 8·7. $C_{21}H_{20}ON_2$ requires N, 8·8%).

The method first described was applied to the preparation of 2-*phenyl*-3-p-*methoxyphenyl*-5-*methylindole*, long prisms, m. p. 150—151° (Found : N, 4·8. $C_{22}H_{19}ON$ requires N, 4·5%), and of 2-*phenyl*-

3-p-*methoxyphenyl*-1-*methylindole*, needles, m. p. 131—133° (Found: N, 4·6%). The former was also synthesised by boiling phenyl *p*-methoxybenzyl ketone with *p*-tolylhydrazine in alcoholic hydrochloric acid for 3 hours; and for comparison 3-*phenyl*-2-p-*methoxyphenylindole* was prepared in like manner from *p*-methoxyphenyl benzyl ketone: needles, m. p. 140—142°, depressed by admixture with its isomeride (Found: N, 4·3%). The latter was synthesised by methylating (IV) as follows: To the indole (0·4 g.) in lukewarm acetone (6 c.c.) were added excess of powdered potassium hydroxide and, portionwise, methyl sulphate (1 c.c.). After 45 mins., the mixture was treated with water, and the product extracted with benzene and crystallised from alcohol.

When (II) was heated with pyridine hydrobromide in pyridine in a sealed tube at 200°, the only isolable product crystallised from alcohol in nitrogen-free plates, m. p. 94—96°; the related *p*-toluidinoketone similarly gave a nitrogen-free substance, m. p. 92—94°, mixed m. p. with its analogue, 79—85°.

The authors are indebted to the Carnegie Trust for the Universities of Scotland for a Scholarship (to R. M. C.), and to Mr. J. M. L. Cameron for micro-analyses.

UNIVERSITY OF GLASGOW. [*Received, November 4th*, 1946.]

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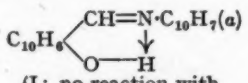
195. *Experiments with Diazomethane and its Derivatives. Part XIII.* Action of Diazomethane on Hydroxyanils.*

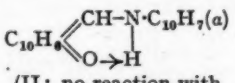
By ALEXANDER SCHÖNBERG, AHMED MUSTAFA, and (in part) MUSTAFA KAMAL HILMY.

The *o*-hydroxyanils listed in Table I are *stable* or very resistant towards *ethereal* diazomethane solution, but, reacting in the ketonic form, they yield coumaran derivatives (listed in Table II) when treated with diazomethane *in the presence of methyl alcohol*; scheme (C) illustrates the proposed reaction mechanism. The stability towards ethereal diazomethane is believed to be due to the fact that in ethereal solution the anils do not contain a free hydroxyl group, but a chelate ring system (I or II), and that they react with methyl alcohol with formation of an intermolecular hydrogen bridge and the opening of the chelate ring system (III). The importance of the above findings for the theory of chelation is stressed.

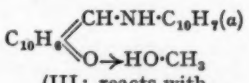
THIS paper deals with the remarkable behaviour of a number of anils (see Table I) derived from *o*-hydroxyaldehydes which were found to be stable towards diazomethane in ethereal solution, but reacted with it in the presence of methyl alcohol. By analogy with our previous findings (Schönberg and Mustafa, *J.*, 1946, 746), this is ascribed to the fact that these *o*-hydroxyanils are not true *o*-hydroxy-compounds but resonance hybrids having the hydrogen bridge (see I and II); when, however, methyl alcohol is present, the six-membered ring is opened and the ketonic



(I; no reaction with diazomethane.)



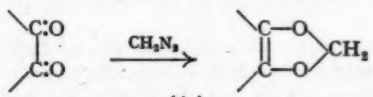
(II; no reaction with diazomethane.)



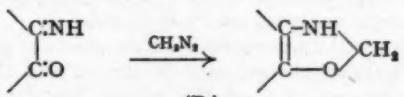
(III; reacts with diazomethane.)

form (III) is established. The differential behaviour of substances listed in Table I towards diazomethane in ethereal and in methyl-alcoholic solution thus constitutes an additional criterion for the existence of chelation.

The anils mentioned above, in the presence of methyl alcohol, have the nature of compounds related to *o*-quinones and *o*-quinoneimines, which react with diazomethane to form five-membered heterocyclic compounds [see Arndt, Amende, and Ender, *Monatsh.*, 1932, **59**, 202; Fieser and Hartwell, *J. Amer. Chem. Soc.*, 1935, **57**, 1479; Schönberg and Mustafa, *loc. cit.*, in the case of (A), and Schönberg and Awad, *loc. cit.*, in the case of (B)]. By analogy, it would



(A.)

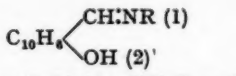


(B.)

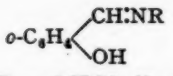
be expected that benzocoumaran derivatives should be obtained when (III) and its analogues are treated with diazomethane in the presence of methyl alcohol, and this is indeed the case (*e.g.*, formation of VII*a*).

* For earlier papers (not numbered) by Schönberg and his co-workers on the action of diazomethane and its derivatives on organic substances, see *Ber.*, 1929, **62**, 440, 1663; 1930, **63**, 3102; 1931, **64**, 1390, 2324, 2577; 1932, **65**, 289; 1933, **66**, 246; *Annalen*, 1930, **483**, 176; *J.*, 1941, 348; *J.*, 1946, 746; this vol., in the press.

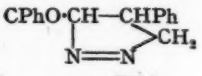
TABLE I.



[IV*a*, R = $C_{10}H_7(\alpha)$; IV*b*, R = $C_{10}H_7(\beta)$; IV*c*, R = $C_6H_3Me_2(2:3)$; IV*d*, R = $C_6H_3Me_2(2:4)$; IV*e*, R = $C_6H_3Me_2(2:5)$.]

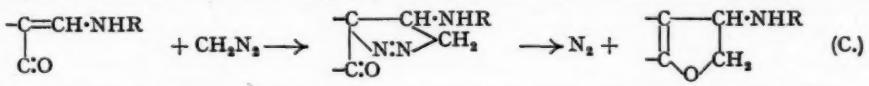


[V; R = $C_6H_3Me_2(2:5)$.]



(VI.)

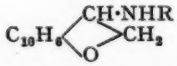
Mechanism of the Formation of the Coumaran Derivatives.—We believe that reaction occurs according to (C): similar schemes are proposed for the above-mentioned actions of diazomethane



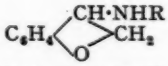
(C.)

on *o*-quinones (1 : 2-diketones; *e.g.*, benzil) or *o*-quinoneimines; compare also the formation of (VI) from benzylideneacetophenone and diazomethane (Smith and Prings, *J. Org. Chem.*, 1937, **2**, 23).

TABLE II.



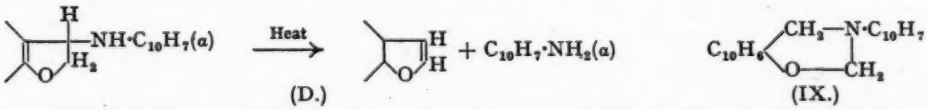
[VII *a*, *b*, *c*, *d*, *e*; R as in corresponding (IV).]



[VIII; R as in (V).]

Constitution of the Products listed in Table II.—These products are of an analogous structure; 3-(α-*naphthylamino*)-4 : 5-*benzocoumaran* (VII*a*) is taken as an example. Its constitution is based on three facts: (*a*) the analogy of its formation (see A and B); (*b*) its properties; (*c*) the fact that no other formula can be proposed which fits the physical and chemical properties of the substance.

In contrast to (IV*a*), (VII*a*) is colourless, in agreement with the proposed formula [reaction has taken place involving the chromophoric system in (III)]; (VII*a*) has no methoxyl group and has one active hydrogen atom (the same holds true for all substances listed in Table II). When it is heated at 250°, it affords α-naphthylamine in addition to a resin, believed to be the polymerisation product of benzocoumarone (see D); the reaction product from (IV*a*) and diazomethane cannot therefore contain a tertiary nitrogen atom, for such a compound (*e.g.*, IX) cannot give α-naphthylamine on pyrolysis.



(D.) (IX.)

The compound (VII*a*) was recovered unchanged when treated with phenylmagnesium bromide followed by hydrolysis; it does not react with diazomethane. The substances listed in Table II have basic properties; *e.g.*, 3-(*p*-2-xylidino)coumaran (VIII) reacts with gaseous hydrogen chloride to form the corresponding hydrochloride. (VII*a*) is completely different from the yellow 2-methoxynaphthylmethylene-α-naphthylamine (*O*-methyl ether of IV*a*); the nature of the latter is established by the fact that it is obtained by the action of methyl sulphate on the sodium salt of 2-hydroxynaphthylmethylene-α-naphthylamine (IV*a*) and by condensation of 2-methoxy-1-naphthaldehyde with α-naphthylamine. The same is true in the case of the β-naphthyl derivative (IV*b*). The substances listed in Table II are all solids, except (VIII), which was analysed as its *hydrochloride*.

Action of Diazomethane on the Anils of p-*Hydroxyaldehydes.*—It was found that 4-hydroxynaphthylmethylene-α-naphthylamine and the corresponding β-naphthyl derivative react with diazomethane to form the known 4-methoxyl derivatives. This action took place even in ethereal diazomethane solution, which was to be expected since in these *p*-hydroxy-compounds the hydroxyl groups are free, no chelation being possible.

EXPERIMENTAL.

The ethereal diazomethane solution was prepared by the action of aqueous potassium hydroxide on nitrosomethylurethane followed by distillation (*Org. Synth.*, Vol. 15, p. 3).

Action of Ethereal Diazomethane Solution on p-*Hydroxybenzylidene-α- and -β-naphthylamine.*—These compounds (Senier and Forster, *J.*, 1914, **105**, 2470) were converted into the corresponding *O*-methyl ethers by the action of an ethereal diazomethane solution in the cold (Found, respectively: C, 82·3;

H, 5·9; N, 5·7; and C, 82·5; H, 5·8; N, 5·8. Calc. for $C_{18}H_{15}ON$: C, 82·8; H, 5·7; N, 5·4%). Further identification was carried out by mixed m. p. determination with authentic specimens of *p*-methoxybenzylidene-α- (Pope and Fleming, *J.*, 1908, **93**, 1916) and -β-naphthylamine (Steinhart, *Annalen*, 1887, 241, 341), respectively.

2-Hydroxy-1-naphthylmethylene-o-3-xylidine (IV*c*) was obtained by the condensation of equimolecular amounts of 2-hydroxy-1-naphthaldehyde and *o*-3-xylidine in yellow needles; m. p. 153° (Found: C, 83·1; H, 6·2; N, 5·3. $C_{19}H_{17}ON$ requires C, 82·9; H, 6·2; N, 5·1%). The condensation was carried out as described by Senier and Clarke (*J.*, 1911, **99**, 2084) for the synthesis of (IV*d*).

o-Hydroxyanils which resist the Action of an Ethereal Solution of Diazomethane.—Ethereal solutions of 1 g. each of (IV*a*) (Bartsch, *Ber.*, 1903, **36**, 1975), (IV*b*) (*idem*, *ibid.*), (IV*c*), (IV*d*) (Senier and Clarke, *loc. cit.*), (IV*e*) (*idem*, *loc. cit.*), and (V) were treated with excess of cold diazomethane (prepared from nitrosomethylurethane, 8 g.), and the mixture left for 48 hours at 0°. The ether was then evaporated off, and in every case the crude products showed the properties of the starting materials and after recrystallisation showed the same m. p. and mixed m. p.

Action of Diazomethane on o-Hydroxyanils in the Presence of Methyl Alcohol.—(*a*) 2-Hydroxy-1-naphthylmethylene-α-naphthylamine (IV*a*) (Bartsch, *loc. cit.*) (1 g.) in cold methyl alcohol (10 c.c.) was treated as in the preceding paragraph, fresh amounts of ethereal diazomethane being added during the 48 hours. The methyl alcohol and ether were evaporated off, and the solid residue was crystallised from benzene–light petroleum (b. p. 30—50°), forming colourless crystals, m. p. 169°. *3-(α-Naphthylamino)-4 : 5-benzocoumaran* (VII*a*) is insoluble in hot water, soluble in hot benzene, hot ethyl alcohol, and cold ether, and gives a yellow colour with concentrated sulphuric acid (Found: C, 85·4; H, 5·5; N, 4·2; active hydrogen, 0·34. $C_{23}H_{17}ON$ requires C, 84·9; H, 5·5; N, 4·5; active hydrogen, 0·32%). When crystallised from hot glacial acetic acid, it gave colourless crystals of the *acetyl* derivative, m. p. 225° (Found: C, 77·4; H, 5·9. $C_{24}H_{21}O_3N$ requires C, 77·6; H, 5·6%); when the solution of this derivative in hot water was treated with aqueous ammonia, (VII*a*) was recovered (m. p. and mixed m. p.).

(*b*) Similarly, *3-(β-naphthylamino)-4 : 5-benzocoumaran* (VII*b*) was obtained from 2-hydroxy-1-naphthylmethylene-β-naphthylamine (IV*b*) in almost colourless crystals, m. p. 190°. It is soluble in hot benzene and ethyl alcohol and gives a yellowish-green colour when treated with concentrated sulphuric acid (Found: C, 84·8; H, 5·7; N, 4·5%). It was crystallised from benzene–light petroleum (b. p. 30—50°).

(*c*) The action of ethereal diazomethane in the presence of methyl alcohol on 2-hydroxy-1-naphthylmethylene-*o*-3-xylidine (IV*c*) gave colourless crystals of *3-(o-3-xylidino)-4 : 5-benzocoumaran* (VII*c*), readily crystallised from benzene, m. p. 173°; soluble in ether and hot ethyl alcohol, difficultly soluble in light petroleum (b. p. 50—60°) (Found: C, 83·1; H, 6·6; active hydrogen, 0·36. $C_{20}H_{19}ON$ requires C, 83·0; H, 6·6; active hydrogen, 0·35%).

(*d*) Similarly, 2-hydroxy-1-naphthylmethylene-*m*-4-xylidine (IV*d*) was treated with ethereal diazomethane in the presence of methyl alcohol, and *3-(m-4-xylidino)-4 : 5-benzocoumaran* (VII*d*) obtained in colourless crystals; it is readily crystallised from benzene or methyl alcohol, m. p. 200°, difficultly soluble in ether, soluble in hot benzene (Found: C, 82·7; H, 6·2; N, 4·9. $C_{20}H_{19}ON$ requires C, 83·0; H, 6·6; N, 4·8%).

(*e*) In the usual manner (IV*e*) was converted into *3-(p-xylidino)-4 : 5-benzocoumaran* (VII*e*), which formed colourless crystals from benzene–light petroleum (b. p. 50—70°), m. p. 162—163° (yellow-brown melt), readily soluble in ether and benzene and difficultly soluble in light petroleum (b. p. 50—70°) (Found: C, 82·8; H, 6·1; N, 5·3; active hydrogen, 0·36%).

(*f*) Salicylidene-*p*-xylidine (V) (Senier and Shepheard, *J.*, 1909, **95**, 443) was treated similarly; evaporation of the ether and methyl alcohol gave an oily product. Its ethereal solution on treatment with a stream of dry hydrogen chloride gave the *hydrochloride* of 3-(*p*-xylidino)-4 : 5-coumaran (VIII) in colourless crystals, m. p. 183° (not sharp); difficultly soluble in benzene and cold ethyl alcohol, soluble in hot water (Found: C, 69·9; H, 6·7; N, 5·1; Cl, 12·8. $C_{16}H_{16}ONCl$ requires C, 69·8; H, 6·5; N, 5·1; Cl, 12·8%).

Preparation of o-Methoxyanils.—The following *O*-methyl ethers of *o*-hydroxyanils were prepared by condensation of equimolecular amounts of 2-methoxy-1-naphthaldehyde (Barger and Starling, *J.*, 1911, **99**, 2032) and the corresponding aromatic amine (cf. Steinhart, *loc. cit.*). The reaction mixture in alcohol was heated under reflux for 2 hours; on cooling, and if necessary on concentration, the methyl ethers of the hydroxyanils separated out. Colours obtained with concentrated sulphuric acid are given in parenthesis after the m. p.

2-Methoxy-1-naphthylmethylene-α-naphthylamine was obtained in brownish-yellow crystals from ethyl alcohol, m. p. 143—144° (red); it is readily crystallised from hot benzene (Found: C, 84·3; H, 5·6; N, 4·9; OMe, 9·4. $C_{23}H_{17}ON$ requires C, 84·9; H, 5·5; N, 4·5; OMe, 9·9%). The *β-naphthyl* analogue formed yellow crystals, readily crystallised from ethyl alcohol, m. p. 123° (reddish-orange) (Found: C, 84·3; H, 5·0; N, 4·8%). The *o-3-xylidine* compound formed yellow crystals from ethyl alcohol, m. p. 120° (orange-yellow), soluble in hot ethyl alcohol and benzene (Found: C, 83·2; H, 6·8; N, 4·7. $C_{20}H_{19}ON$ requires C, 83·0; H, 6·6; N, 4·8%). The *m-4-xylidine* analogue crystallised from methyl alcohol in yellow crystals, m. p. 71° (orange), easily soluble in benzene (Found: C, 83·1; H, 6·4; N, 4·8%). The *p-xylidine* compound formed yellow crystals from methyl alcohol, m. p. 117° (orange) (Found: C, 82·4; H, 6·8; N, 4·9%).

Action of Methyl Sulphate on 2-Hydroxy-1-naphthylmethylene-β-naphthylamine (IV*b*).—A suspension of (IV*b*) (1 g.) in hot methyl alcohol (15 c.c.) was treated gradually with methyl sulphate (about 2 c.c.), followed by addition of a methyl-alcoholic solution of potassium hydroxide till alkaline. The mixture was set aside at room temperature for 2 hours, poured into water, extracted with ether, and crystallised from ethyl alcohol; it formed yellow crystals, m. p. 123° (red-brown melt), not depressed when admixed with a specimen of 2-methoxy-1-naphthylmethylene-β-naphthylamine prepared as above. The α-analogue was similarly obtained in yellow crystals, m. p. 143°, not depressed when admixed with a specimen of 2-methoxy-1-naphthylmethylene-α-naphthylamine prepared as above.

Phenylmagnesium Bromide and 3-(α-Naphthylamino)-4 : 5-benzocoumaran.—The benzocoumaran

(VII*a*) was treated with excess of phenylmagnesium bromide in ether–benzene, heated under reflux for 2 hours, and left overnight at room temperature. On hydrolysis, the starting substance was obtained unchanged or almost unchanged.

Action of Heat on 3-(α-*Naphthylamino*)-4 : 5-*benzocoumaran*.—The coumaran (VII*a*) (1 g.) was heated in a stream of dry carbon dioxide for ½ hour (bath temp., 250°). An almost colourless oil distilled over, which, on cooling, followed by extraction with hot light petroleum (b. p. 30—50°) and evaporation of the latter, gave colourless crystals of α-naphthylamine (m. p. and mixed m. p.). The part insoluble in the light petroleum was a resin which could not be identified.

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196. *The Quantitative Determination of Galactose, Mannose, Arabinose, and Rhamnose.*

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Methods are described for the quantitative analysis of mixtures of galactose, mannose, arabinose, and rhamnose, which may occur amongst the hydrolysis products of plant gums. Galactose is estimated as its phenylmethylhydrazone, mannose as its phenylhydrazone, and arabinose as its benzoylhydrazone. The methods are accurate to within 9 mg. on weights above 0·1 g. Rhamnose can be determined as the benzoylhydrazone with an accuracy of ±30 mg. on weights above 0·25 g.

THE plant gums are complex polysaccharides which contain a variety of sugar residues and amongst the products of hydrolysis galactose, mannose, arabinose, and rhamnose frequently occur. The quantitative determination of these sugars is a matter of some difficulty, the more so when they are admixed with other sugars and acids formed during the hydrolysis of the gums. We have carried out by the standard mucic acid method a large number of determinations of galactose in mixtures of sugars obtained from the hydrolysis of plant products, and have found the method inadequate, especially when only small quantities of material are available and when *d*-galacturonic acid and *l*-galactose are present. Other methods which have been described are (1) the fermentation method using special strains of yeast (Wise and Appling, *Ind. Eng. Chem. Anal.*, 1944, **16**, 28), and (2) a method in which the insoluble phenylmethylhydrazone of galactose is weighed. This latter method has been used by Neuberg (*Biochem. Z.*, 1907, **3**, 519), Lüdtke (*Biochem. Z.*, 1919, **212**, 419), Neuberg and Schweitzer (*Monatsh.*, 1937, **71**, 46), and Freeman, Challinor, and Willis (*Biochem. J.*, 1940, **34**, 316). These authors converted pure galactose into its phenylmethylhydrazone under standard conditions and used a factor for the conversion of the weight of derivative isolated into the weight of galactose in solution. This method, however, gives accurate results only if the amounts of galactose in the control and in the unknown solution are identical. To avoid the necessity of carrying out a control estimation on each occasion we have determined the yields, under standard conditions, of the phenylmethylhydrazone of galactose obtained from various amounts of galactose (Table I). From the results a graph was constructed which showed that the relationship between galactose and the yields of galactose phenylmethylhydrazone was linear even when glucose, xylose, rhamnose, and glucuronic acid were present. Mannose and arabinose interfere with the estimation, but the difficulties thus arising can be readily circumvented. Mannose can be estimated by the phenylhydrazine method (Bourquelot and Herissey, *Compt. rend.*, 1899, **129**, 339; see below) and can be removed by fermentation. Arabinose cannot be removed by fermentation but can be estimated by means of diphenylhydrazine (Neuberg, *Ber.*, 1900, **33**, 2243; Wise and Paterson, *Ind. Eng. Chem.*, 1930, **22**, 365) or by boiling with 12% hydrochloric acid and estimation of the furfural evolved. Since the precipitation of arabinose with phenylmethylhydrazine appears to be nearly quantitative in the presence of galactose, an estimate of the galactose present can be made after deducting the weight of phenylmethylhydrazone formed from the arabinose, the amount of which has been estimated by another method.

The quantitative estimation of arabinose in the presence of galactose is a matter of some difficulty since most reagents which give insoluble derivatives with arabinose also give insoluble derivatives with galactose, *e.g.*, phenylmethylhydrazine and phenylbenzylhydrazine. A reagent which does not possess this disadvantage is benzoylhydrazine. This reagent also has the advantage of ease of preparation and of stability (Fischer and Paulus, *Arch. Pharm.*, 1935, 83; Militzer, *J. Chem. Educ.*, 1941, 25). In this estimation the mixture of sugars containing

arabinose (50 mg. in 500 mg.) is dissolved in water (2 c.c.) and a solution of benzoylhydrazine in alcohol (10 c.c.) is added; after two days the insoluble derivative is filtered off, dried, and weighed. Of many sugars examined the only one which interfered with this estimation was rhamnose, when present in quantities of over 300 mg. The standardisation was carried out as described above (see Table II *a* and *b*), and gave a method of estimating arabinose accurate to within 9 mg. on 100 mg. when using weights of arabinose above 0·1 g. In the absence of arabinose this reagent can be used for the characterisation and quantitative estimation of rhamnose (see Table III).

The estimation of mannose with phenylhydrazine has already been described (Bourquelot and Herissey, *Compt. rend.*, 1899, **129**, 339). By adoption of the modified procedure described in the experimental section this method can be used for the estimation of mannose with an accuracy of approximately ± 3 mg. on quantities of 100 mg. and over of mannose. The method was standardised in a manner similar to that described for galactose and arabinose (Table IV), and it was found that no interference was caused by glucose, galactose, rhamnose, or arabinose.

Experimental.

Galactose. Reagent and Method of Analysis.—1-Phenyl-1-methylhydrazine (25 g.) was mixed with absolute alcohol (100 c.c.) containing glacial acetic acid (3 c.c.). The reagent was kept in a tightly stoppered brown glass bottle at 0°.

To the sugar sample (containing not more than 1·4 g. of sugars) dissolved in water (10 c.c.) the above reagent (10 c.c.) was added and the mixture was kept in a tightly stoppered flask at 33° for 12 hours with occasional shaking. It was then cooled to 0° for 9 hours and the crystals (m. p. 186°) were collected in a tared Gooch crucible, washed with ice-cold ethyl alcohol (10 c.c.), dried at 100° for 30 minutes, and weighed. The yields of phenylmethylhydrazone obtained from various weights of galactose with and without the presence of other sugars are given in Table I. From these results it can be seen that the method is accurate to within ± 3 mg. on amounts above 0·1 g.

Table I.

Galactose (g.).	Sugars added (g.).	Yield of phenylmethyl hydrazone (g.).	Galactose (from graph) (g.).	Error (g.).	Error calc. on original wt. of galactose (%).
0·037	—	0·039	0·039	+0·002	+ 5·4
0·077	—	0·096	0·077	nil	nil
0·126	—	0·177	0·132	+0·006	+ 4·8
0·260	—	0·367	0·263	+0·003	+ 1·2
0·426	—	0·615	0·433	+0·007	+ 1·7
0·711	—	1·036	0·719	+0·008	+ 1·1
1·394	—	2·042	1·403	+0·009	+ 0·7
0·184	Mannose, 0·500	1·020 [1]	0·178	−0·006 [1]	− 3·3
0·231	Arabinose, 0·500	1·030 [2]	0·204	−0·027 [2]	−12·0
0·225	Xylose, 0·500	0·320	0·231	+0·006	+ 2·6
0·202	Rhamnose, 0·500	0·281	0·205	+0·003	+ 1·5
0·232	Glucuronic acid, 0·500	0·320	0·231	−0·001	− 0·5
0·296	Glucose, 0·500	0·405	0·289	−0·007	− 2·4

[1] 0·245 G. of mannose phenylmethylhydrazone.
[2] 0·283 G. of *l*-arabinose phenylmethylhydrazone.

From these figures the equation $y = 0{\cdot}673x + 0{\cdot}013$ can be deduced where y corresponds to the weight of galactose giving a weight x of phenylmethylhydrazone.

Arabinose. Reagent and Method of Analysis.—Benzoylhydrazine, recrystallised from water and having m. p. 112—113° (25 g.), was dissolved in 95% alcohol (500 c.c.) and the solution was kept in a stoppered bottle until required. The sugar sample containing between 50 and 500 mg. of arabinose was dissolved in water (2 c.c.) in a 50 c.c. stoppered flask, and the reagent (10 c.c.) then added. The mixture was kept with occasional shaking at 20° for 24 hours and then at −3° for 22 hours. The crystalline residue, m. p. 186—190° (decomp.), was collected in a tared Gooch crucible, washed with ice-cold alcohol (10 c.c.), dried at 100° for ½ hour and weighed. It will be seen (Table II*a*) that of the sugars glucose, mannose, xylose, galactose, glucurone, and rhamnose, only the last named interfered with the estimation and then only when present in amounts above 300 mg. The relationship between the weight of arabinose and the yield of derivative was linear and fitted the equation $y = 0{\cdot}555x + 0{\cdot}022$ where y is the weight of arabinose corresponding to a weight x of derivative isolated.

d-Arabinose benzoylhydrazone was prepared, as described above, from *d*-arabinose and benzoylhydrazine, m. p. 186° (decomp.). *d*-Glucose gave with benzoylhydrazine a *derivative* {m. p. 176—179° (decomp.), $[\alpha]_D^{20°}$ $+15° \xrightarrow{17 \text{ hrs.}} -23°$ in water} which was much more soluble than the derivative of arabinose and rhamnose; it did not interfere with the estimation of these two sugars (Found: C, 52·4; H, 6·0; N, 9·6. $C_{19}H_{18}O_6N_2$ requires C, 52·4; H, 6·0; N, 9·4%).

In the second method of estimation of arabinose, an aqueous solution of benzoylhydrazine saturated at 20° (*ca.* 4·3 g./100 c.c. of water) was used as a reagent. The derivative is more soluble in this reagent

but separates in a more easily filtered form. Since the reagent contains no alcohol, alcohol-insoluble materials such as oligosaccharides and the barium salts of uronic acids remain in solution during the reaction and do not contaminate the precipitate of arabinose benzoylhydrazone. The dry, water-soluble product to be analysed, containing between 50 and 150 mg. of arabinose, is dissolved in the reagent (5 c.c.) and kept at 30° for 48 hours and then cooled to 0° for 2 hours. The crystalline precipitate is filtered off, washed with 10 c.c. of 95% alcohol, and dried at 100° to constant weight. If the residue contains between 150 and 400 mg. of arabinose, more of the reagent (10 c.c.) is used. The derivative is isolated and weighed as above. From the results obtained the equation $y = 0{\cdot}67x + 0{\cdot}010$ can be deduced where y is the weight of arabinose required to give a weight x of derivative (see Table II*b*).

TABLE II*a*.

Arabinose (g.).	Other sugars (g.).	Derivative of arabinose.	Arabinose from equation.	Error (g.).	Error calc. on wt. of arabinose taken (%).
0·212	—	0·310	0·194	−0·018	−8·5
0·234	Rhamnose, 0·087	0·362	0·223	−0·011	−5·0
0·206	Galactose, 0·071	0·297	0·187	−0·019	−9·2
0·215	Mannose, 0·108	0·319	0·199	−0·016	−7·4
0·294	—	0·478	0·288	−0·006	−2·1
0·344	—	0·574	0·341	−0·003	−0·9
0·402	—	0·683	0·401	−0·001	−0·3
0·243	Glucurone, 0·240	0·376	0·231	−0·012	−5·0
0·257	—	0·435	0·264	+0·007	+2·8
0·389	Rhamnose, 0·332	0·656	0·386	−0·003	−0·8
0·347	—	0·592	0·351	+0·004	+1·2
0·410	Galactose, 0·175	0·701	0·411	+0·001	+0·3
0·447	—	0·768	0·449	+0·002	+0·5
0·483	—	0·827	0·481	−0·002	−0·4
0·055	—	0·054	0·052	−0·003	−5·5
0·072	—	0·083	0·068	−0·004	−5·6
0·107	—	0·162	0·112	+0·005	+4·5
0·178	—	0·297	0·191	+0·013	+7·4
0·154	—	0·254	0·163	+0·009	+5·8
0·198	—	0·337	0·209	+0·011	+5·6
0·055	Rhamnose, 0·350	0·234	0·152	+0·097	Interferes
0·236	Xylose, 0·331; Rhamnose, 0·041; Mannose, 0·080	0·389	0·238	+0·002	+0·9
0·120	Glucose, 0·372	0·174	0·119	−0·001	−0·8
0·120	Glucose, 0·371	0·166	0·114	−0·006	−5·0
0·111	Mannose, 0·397	0·148	0·104	−0·007	−6·3
0·067	—	0·081	0·067	nil	nil
0·112	—	0·166	0·114	+0·002	+1·8
0·271	—	0·462	0·279	+0·008	+2·9
0·394	—	0·687	0·404	+0·010	+2·5
0·421	—	0·724	0·424	+0·003	+0·7
0·088	—	0·122	0·090	+0·002	+2·3
0·218	Mannose, 0·308	0·363	0·224	+0·006	+2·8
0·172	—	0·278	0·176	+0·004	+2·3
0·266	Rhamnose, 0·358	0·603	0·357	+0·091	Interferes
0·446	—	0·770	0·450	+0·004	+0·9
0·361	—	0·617	0·365	+0·004	+1·1
0·160	Xylose, 0·321	0·264	0·169	+0·009	+5·6
0·129	Galactose, 0·372	0·175	0·119	−0·010	−8·0

TABLE II*b*.

Arabinose (g.).	Sugar impurity (g.).	Benzoyl-hydrazone found (g.).	Arabinose (from equation) (g.).	Error (g.).	Error calc. on wt. of arabinose taken (%).
0·068		0·062	0·052	−0·016	−23·5
0·079	—	0·088	0·069	−0·010	−12·7
0·116	—	0·164	0·120	+0·004	+ 3·4
0·185	—	0·286	0·202	+0·017	+ 9·2
0·213	—	0·314	0·220	+0·007	+ 3·3
0·173	Rhamnose, 0·190	0·202	0·147	−0·026	−15·0
0·268	—	0·389	0·271	+0·003	+ 1·1
0·384	Xylose, 0·190	0·559	0·385	+0·001	+ 0·3
0·412	—	0·625	0·428	+0·016	+ 3·9

Rhamnose.—Rhamnose cannot be so successfully estimated as arabinose by the use of benzoylhydrazine, owing to the greater solubility of the rhamnose derivative and the interfering effect of small

quantities of arabinose. The sugar sample (250 to 600 mg. in 2 c.c. water) was mixed with saturated alcoholic benzoylhydrazone solution (10 c.c.) and the solution kept at 30° for 41 hours. After 17 hours the solution was seeded with a trace of the rhamnose derivative. After 41 hours the solution was cooled to −3° and the product filtered off and washed with 95% alcohol (30 c.c. in all). To avoid charring it was necessary to dry the product first in a desiccator and then at 90° for 1 hour. From the yields of derivative (see Table III) the equation $y = 0{\cdot}482x + 0{\cdot}217$ was deduced, where y is the weight of rhamnose hydrate which will give a yield, x, of rhamnose benzoylhydrazone. The rhamnose benzoylhydrazone separated as very fine white crystals which could be recrystallised from methyl alcohol. The derivative separated from methyl alcohol as long white needles, m. p. 180° (decomp.) (Found: C, 55·5; H, 6·4; N, 10·0. $C_{13}H_{18}O_5N_2$ requires C, 55·3; H, 6·4; N, 9·9%).

TABLE III.

l-Rhamnose hydrate taken (g.).	Sugar impurity (g.).	Yield of benzoyl-hydrazone (g.).	Rhamnose hydrate (from equation) (g.).	Error (g.).	Error calc. on wt. of rhamnose taken (%).
0·578	—	0·679	0·544	−0·034	− 5·9
0·451	—	0·529	0·471	+0·020	+ 4·5
0·349	—	0·351	0·386	+0·037	+10·7
0·210	—	0·026	0·230	+0·020	+ 9·6
0·270	—	0·191	0·309	+0·039	+14·4
0·322	—	0·271	0·347	+0·025	+ 7·8
0·370	—	0·326	0·374	+0·004	− 1·1
0·408	—	0·385	0·379	−0·029	− 7·1
0·470	—	0·471	0·444	−0·026	− 5·5
0·503	—	0·481	0·449	−0·054	−10·7
0·213	—	0·002	0·218	+0·005	+ 2·3
0·338	—	0·234	0·330	−0·008	− 2·4
0·256	—	0·086	0·258	+0·002	+ 0·8
0·251	—	0·162	0·295	+0·044	+17·5
0·310	Glucose, 0·470	0·257	0·341	+0·031	+10
0·464	—	0·467	0·442	−0·022	− 4·7
0·554	—	0·605	0·508	−0·046	− 8·3

Mannose. Reagent and Method of Analysis.—Phenylhydrazine (redistilled) (25 c.c.) was mixed with absolute alcohol (100 c.c.) containing glacial acetic acid (3 c.c.). The mixture was kept at 0° in a well-stoppered, dark bottle.

The sugar sample was dissolved in water (10 c.c.), the above reagent (10 c.c.) added, and the mixture kept in a well-stoppered flask at 32° for 15 hours, with occasional shaking. It was then cooled to 0° for 12 hours, and the phenylhydrazone was filtered off, washed with ice-cold alcohol (10 c.c.), dried at 100° for 30 minutes, and weighed. The yields of phenylhydrazone from various weights of mannose, together with the effect of various other sugars on the estimation, are given in Table IV.

TABLE IV.

Mannose (g.).	Sugar impurity (g.).	Yield of hydrazone (g.).	Mannose (from graph) (g.).	Error (g.).
0·026	—	nil	nil	−0·026
0·051	—	0·011	0·033	−0·018
0·100	—	0·114	0·100	nil
0·203	—	0·277	0·205	+0·002
0·401	—	0·573	0·400	−0·001
0·601	—	0·890	0·610	+0·009
1·001	—	1·488	1·003	+0·002
0·221	Glucose, 0·500	0·310	0·228	+0·007
0·260	Arabinose, 0·500	0·355	0·258	−0·002
0·214	Galactose, 0·500	0·300	0·220	+0·006
0·225	Rhamnose, 0·500	0·298	0·219	−0·006
0·205	Glucuronic acid, 0·500	0·280	0·207	+0·002

These figures fit the equation $y = 0{\cdot}652x + 0{\cdot}031$ where y is the weight of mannose giving a weight x of mannose phenylhydrazone.

From these results it can be seen that glucose, arabinose, galactose, rhamnose, and glucuronic acid do not interfere with the estimation of mannose, and that it is possible to carry out the estimation to within ±3 mg. on amounts above 100 mg.

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197. *A Synthesis of Cytidine.*

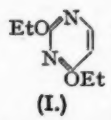
By G. A. Howard, B. Lythgoe, and A. R. Todd.

Hydrogenolysis of 1 : 2 : 3-triacetyl 5-trityl *d*-ribofuranose gives a syrupy 1 : 2 : 3-triacetyl *d*-ribofuranose converted on acetylation into the crystalline 1 : 2 : 3 : 5-*tetra-acetyl* d-*ribofuranose*. Treatment of the latter with liquid hydrogen bromide gave crude acetobromoribofuranose which was used directly to prepare *theophylline-7-β-d-ribofuranoside*. By reaction of the acetobromoribofuranose with 2 : 6-diethoxypyrimidine, followed by treatment of the product with methanolic ammonia, 3-*β*-*d*-ribofuranosidocytosine has been synthesised identical with the natural nucleoside, cytidine.

Methods for the synthesis of nucleosides have been under investigation in this laboratory for some time with a variety of objects in view. On the one hand it was hoped that a successful outcome of the work would render available for biological examination a range of structural analogues of the natural nucleosides as a possible means of elucidating the mode of action of the latter in organised systems; on the other, study of the simpler compounds seemed a necessary preliminary to broader synthetic investigations relating to the co-enzymes and polynucleotides in the molecules of which nucleoside structures are preformed.

In a series of papers in this *Journal* ("Experiments on the Synthesis of Purine Nucleosides," Parts I—XVI, reviewed in *J.*, 1946, 647) we have reported progress made in the development of methods for the synthesis of analogues of adenosine, perhaps the most important of the natural nucleosides. General methods have been made available for the synthesis of 9-glycopyranosido- and 9-glycofuranosido-adenine derivatives, and answers have been provided to certain structural questions on which at the outset there was either no evidence or on which available evidence was not completely rigid. With the major problems of this part of the field approaching, as we hope, a satisfactory solution, it seemed desirable to broaden the scope of the investigations to include compounds of the type of guanosine, the pyrimidine ribosides, and the pyrimidine and purine deoxyribosides. The present communication records experiments which have led to the synthesis of the natural pyrimidine riboside, cytidine.

The problems of synthesis of pyrimidine glycosides have been examined by a number of previous workers. The route which has received most attention depends on the direct introduction of an acetylated glycosyl residue into the nucleus of an appropriate pyrimidine derivative by use of an acetohalogeno-sugar, a method essentially similar to Fischer and Helferich's synthesis of purine glycosides (*Ber.*, 1914, **47**, 210). The early investigators (Fischer and Helferich, *loc. cit.*; Fischer, *Ber.*, 1914, **47**, 1377; Levene and Sobotka, *J. Biol. Chem.*, 1925, **65**, 469) employed, for glycosidisation, pyrimidine derivatives containing substituents such as hydroxyl, to which, as a result of their capacity for prototropic change, the glycosyl residue became attached, so that they were not successful in obtaining heterocyclic *N*-glycosides. This difficulty was overcome by Hilbert and his collaborators, employing 2 : 6-dialkoxypyrimidines, in which tautomerisation possibilities are excluded. Thus interaction of 2 : 6-diethoxypyrimidine (I) and acetobromoglucose gave the tetra-acetyl glucoside (II) which could be converted by methanolic hydrogen chloride into a 3-*d*-glucosidouracil (III; R = OH), or by methanolic ammonia into a 3-*d*-glucosidocytosine (III; R = NH_2) (Hilbert and Johnson, *J. Amer. Chem. Soc.*, 1930, **52**, 4489; Hilbert and Jansen, *ibid.*, 1936, **58**, 60).



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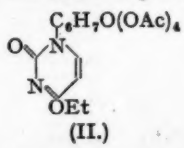

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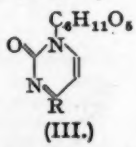


(III.)

Structural analogues of (III) carrying various glycosyl residues have been obtained by this method (Hilbert, *ibid.*, 1937, **117**, 331) including a 3-*d*-ribosidouracil (Hilbert and Rist, *J. Biol. Chem.*, 1937, **117**, 331); all these compounds must, from their mode of preparation, be pyranosides.

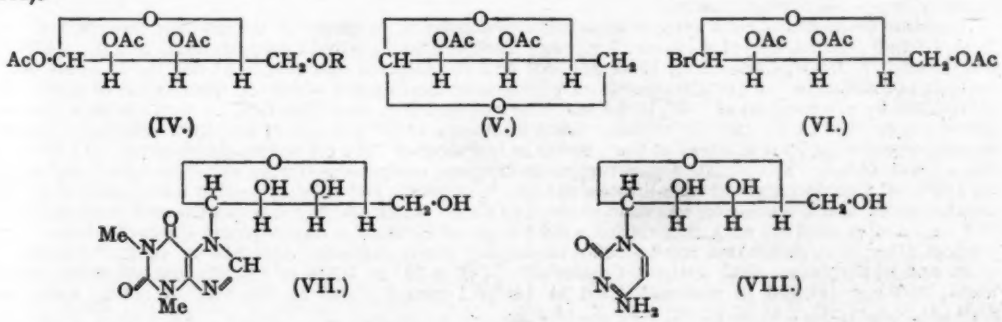
An alternative synthesis of pyrimidine nucleosides may be envisaged involving cyclisation of an appropriate glycosidamino-compound; such a method would be analogous in principle to our method for synthesis of purine-9-glycosides from 5-amino-4-glycosidaminopyrimidine derivatives. If developed, such a method might offer, in comparison with the synthesis from acetohalogeno-sugars, advantages such as the demonstration of the position of the sugar residue in the final product. It was in part this consideration that influenced us in our choice of a route for the synthesis of purine-9-glycosides, but it seemed of less importance in the case of the

pyrimidine nucleosides, since the N_3 location of the sugar residue in uridine has been fully established by Levene and Tipson (*J. Biol. Chem.*, 1934, **104**, 385), and we have shown (Davoll, Lythgoe, and Todd, *J.*, 1946, 833) that in the uracil-*d*-glucoside obtained by Hilbert's method the glucose residue does in fact, as formerly assumed from analogy (Hilbert and Johnson, *loc. cit.*), occupy the same position. We therefore decided in the first instance to attempt the synthesis of cytidine by extending Hilbert's method.

The acetohalogeno-ribofuranose required for this purpose belongs to a class of compounds which in spite of their potential synthetic value have been little explored, mainly because of the inaccessibility of suitable furanose intermediates. In the pentose series no true representative of this class has been obtained, and amongst the hexoses only those derived from galactose (Schlubach and Wagenitz, *Z. physiol. Chem.*, 1932, **213**, 87). Aniline-*d*-ribofuranoside (Berger and Lee, *J. Org. Chem.*, 1946, **11**, 75) seemed at first sight to be a suitable starting material for the preparation of acetobromoribofuranose. It has been stated (*idem*, *ibid.*; Berger, Solmssen, Leonard, Wenis, and Lee, *ibid.*, p. 91) that this compound can be acetylated to a 2 : 3 : 5-triacetyl *d*-ribosidoaniline which yields on careful acidic hydrolysis 2 : 3 : 5-triacetyl *d*-ribofuranose. However, as already recorded by us (Howard, Kenner, Lythgoe, and Todd, *J.*, 1946, 855) the acetylation is accompanied by a change to the isomeric pyranoside, so that in fact the product of the above reaction series is 2 : 3 : 4-triacetyl *d*-ribopyranose.

It was therefore decided to study in more detail the method used by Bredereck, Köthnig, and Berger (*Ber.*, 1940, **73**, 956) in their attempt to obtain acetobromoribofuranose. These investigators prepared 1 : 2 : 3-triacetyl 5-trityl *d*-ribose (IV; R = CPh_3), but attempts at selective removal of the trityl group from this compound were unsuccessful, giving instead of the desired 1 : 2 : 3-triacetyl *d*-ribofuranose (V; R = H) a diacetyl anhydroribose <1 : 5> <1 : 4> (V) owing to simultaneous loss of the acetyl group at C_1. In these experiments hydrogen bromide in acetic acid or aqueous acetic acid was used for fission of the trityl ether linkage, but it is known (*e.g.*, Micheel, *Ber.*, 1932, **65**, 262) that the fission may be effected by hydrogenolysis. By using the latter method we were successful in preparing from (IV; R = CPh_3) a syrupy 1 : 2 : 3-triacetyl *d*-ribofuranose (IV; R = H), in which the terminal location of the free hydroxyl group was shown by its conversion into a syrupy tosyl derivative which readily exchanged its tosyl group for iodine in the Oldham–Rutherford reaction. Further acetylation of (IV; R = H) gave in good yield a crystalline 1 : 2 : 3 : 5-*tetra-acetyl* d-*ribofuranose* (IV; R = Ac). In order to convert this into acetobromoribofuranose we adopted the method used by Schlubach and Wagenitz (*loc. cit.*) for the preparation of acetobromogalactofuranose. Brief treatment of (IV; R = Ac) with liquid hydrogen bromide gave a syrup consisting essentially of the desired acetobromo-compound (VI); on account of its evident lability, isolation of the pure compound was not attempted, the crude product being used directly in glycosidisation experiments.

When allowed to react with a suspension of theophylline silver in dry xylene, triacetyl theophylline-*d*-ribofuranoside was obtained as a gum, which on treatment with methanolic ammonia gave in good yield a crystalline *theophylline*-7-β-d-*ribofuranoside* (VII). The structure of this compound follows from the fact that it reacts with sodium metaperiodate, giving a crystalline α-theophylline-7-α′-hydroxymethyldiglycollic aldehyde identical with that obtained from similar oxidation of theophylline-7-β-*d*-glucopyranoside (Lythgoe and Todd, *J.*, 1944, 592).



These reactions provided satisfactory evidence of the nature of the crude acetobromoribofuranose and we could now proceed to the synthesis of cytidine (VIII). Interaction of 2 : 6-diethoxypyrimidine with (VI) at 65° gave a gummy product which on treatment with methanolic ammonia yielded a mixture of bases, from which cytidine was isolated by recrystallisation of the

picrates and finally of the sulphate. The cytidine sulphate so obtained agreed in composition and physical constants with that isolated from yeast nucleic acid. The Molisch test was negative, but after prolonged heating with the perchloric acid–tryptophan reagent (Cohen, *J. Biol. Chem.*, 1944, **156**, 691) the green colour characteristic of pentoses was slowly developed; natural cytidine sulphate behaved in the same manner. Final confirmation of the identity of the natural and synthetic products was obtained by comparison of their *X*-ray crystal photographs, for which we are indebted to Dr. Clews and Mr. Nicol of the Department of Crystallography.

The work described above represents the first synthesis of a naturally occurring nucleoside. Since it is known that cytidine can be deaminated to give uridine, the work also constitutes a synthesis of uridine, and provides confirmation of the degradative evidence relating to the structures of these two nucleosides.

Experimental.

1 : 2 : 3 : 5-*Tetra-acetyl* d-*Ribofuranose*.—1 : 2 : 3-Triacetyl 5-trityl *d*-ribofuranose (21 g.; Bredereck, Köthnig, and Berger, *loc. cit.*) dissolved in glacial acetic acid (250 c.c.) was hydrogenated at 35° and atmospheric pressure in presence of Adams's palladium oxide (1 g.). After 3 hours 900 c.c. of hydrogen had been absorbed and the filtered solution was evaporated to dryness under reduced pressure. Crystallisation of the residue from alcohol gave triphenylmethane (8 g.), and the mother liquors after evaporation were dissolved in a little chloroform, light petroleum (b. p. 100—120°) was added, and the chloroform was removed by evaporation. The petroleum layer was removed, and the insoluble 1 : 2 : 3-triacetyl *d*-ribose acetylated in the usual way by acetic anhydride in pyridine. The acetylated material, isolated in the usual way, was dissolved in chloroform, washed with aqueous sodium bicarbonate and then with water, and the chloroform was removed from the dried solution under reduced pressure. Distillation of the residue at 100—110° (bath temp.)/10^{-4} mm. gave 1 : 2 : 3 : 5-*tetra-acetyl* d-*ribofuranose* as a syrup which crystallised on standing; m. p. 58°, $[\alpha]_D^{15°}$ +20° (±1°) (*c*, 0·645 in chloroform). Yield, 9 g. (70%) (Found: C, 49·1; H, 5·7. $C_{13}H_{18}O_9$ requires C, 49·2; H, 5·2%).

*Theophylline-7-β-*d*-ribofuranoside*.—Pure anhydrous liquid hydrogen bromide (5 c.c.) was distilled into a Carius tube containing 1 : 2 : 3 : 5-tetra-acetyl *d*-ribose (1·5 g.) and, after being sealed, the tube was kept at room temperature for 10 minutes; dissolution was then complete. The tube was then opened and hydrogen bromide allowed to evaporate at room temperature, and the brown residue was evaporated twice with benzene under reduced pressure at 30° and finally heated to 35° in a high vacuum to remove hydrogen bromide as completely as possible. The crude acetobromoribofuranose so obtained was dissolved in a little xylene and the solution refluxed with a suspension of dry theophylline silver (1·5 g.) in dry xylene (50 c.c.) for 1 hour with exclusion of moisture. Silver bromide was removed from the hot solution, which was allowed to cool and filtered from a little theophylline which had separated. The filtrate was evaporated to dryness under reduced pressure and set aside for 2 days at 0° with methanolic ammonia. Removal of solvents and crystallisation of the residue from water gave *theophylline-7-β-*d*-ribofuranoside* as colourless needles, m. p. 189°, $[\alpha]_D^{15°}$ +27° (±5°) (*c*, 0·257 in water) (Found in material dried at 100° and 0·1 mm.: C, 45·1; H, 5·5; N, 19·7. $C_{12}H_{16}O_6N_4$ requires C, 45·0; H, 5·0; N, 20·0%). Yield, 0·88 g. (60%).

Periodate Oxidation.—The above glycoside (209·2 mg.) was treated with a solution of sodium metaperiodate (208 mg. per 6 c.c. water) and set aside for 24 hours. The crystalline deposit of α-theophylline-7-α′-hydroxymethyldiglycollic aldehyde was collected (140 mg.), and had m. p. 205—206° (decomp.), $[\alpha]_D^{18°}$ −38° (*c*, 0·21 in water) (Found: C, 43·7; H, 4·9. Calc. for $C_{12}H_{14}O_6N_4,H_2O$: C, 43·9; H, 4·9%). Lythgoe and Todd (*loc. cit.*) record for the same compound obtained from theophylline-7-β-*d*-glucopyranoside, m. p. 207—208° (decomp.), $[\alpha]_D^{19°}$ −42°.

In one experiment on the preparation of theophylline-*d*-ribofuranoside by the method described, there was isolated as sole product a *substance* separating from aqueous alcohol as colourless needles, m. p. 193°, $[\alpha]_D^{16°}$ +110° (*c*, 0·254 in water) (Found: C, 45·8; H, 5·0; N, 17·9. $C_{12}H_{16}O_6N_4$ requires C, 46·2; H, 5·1; N, 17·9%). This substance required 1·06 mols. of periodate per mol. for complete oxidation, the oxidised product having $[M]_D^{14°}$ 1·03° (±0·5°) × 10^4. It seems possible that it may be theophylline-7-*d*-α-ribofuranoside.

Cytidine Sulphate.—Crude syrupy acetobromoribofuranose prepared in the manner described above from 1 : 2 : 3 : 5-tetra-acetyl *d*-ribose (5 g.) was dissolved in 2 : 6-diethoxypyrimidine (15 g.; Hilbert and Jansen, *J. Amer. Chem. Soc.*, 1935, **57**, 553) and the solution maintained at 65° for 24 hours with exclusion of moisture. After filtration from a little resin the solution was freed from excess of diethoxypyrimidine by evaporation at 100°/10^{-3} mm. The residual 9 g. were dissolved in methanolic ammonia (40 c.c., saturated at 0°) and the solution was maintained at 80° for 4 days and then evaporated under reduced pressure. To a solution of the residue in hot alcohol (10 c.c.) hot alcoholic picric acid (5 g. in 50 c.c.) was added. The picrate separating on cooling was recrystallised from water, and then had m. p. *ca.* 150°. It was decomposed with dilute sulphuric acid, picric and sulphuric acids were removed in the usual manner, and the solution was concentrated to 5 c.c. After addition of concentrated sulphuric acid (0·7 c.c.) and alcohol (25 c.c.), inoculation with a trace of cytidine suphate caused crystallisation. The product after recrystallisation from alcohol containing dilute sulphuric acid had m. p. 224° (decomp.) alone and in admixture with authentic material. $[\alpha]_D^{19°}$ +35° (*c*, 0·366 in 1% aqueous sulphuric acid). Yield, 350 mg. [Found in material dried at 140°/0·1 mm.: C, 37·2; H, 5·2; N, 14·0. Calc. for $(C_9H_{13}O_5N_3)_2,H_2SO_4$: C, 37·0; H, 4·8; N, 14·2%].

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198. *The Constitution of Cherry Gum. Part II. The Products of Hydrolysis of Methylated Cherry Gum.*

By J. K. N. Jones.

Methylated cherry gum has been hydrolysed and the following products of hydrolysis have been identified: 2 : 3 : 5-trimethyl *l*-arabinose, 2 : 5-dimethyl *l*-arabinose, 2 : 4 : 6-trimethyl *d*-galactose, 2 : 4-dimethyl *d*-galactose, 2 : 3 : 4-trimethyl *d*-glucuronic acid, and 2 : 3-dimethyl *d*-glucuronic acid. Derivatives of *d*-mannose and of *d*-xylose are also present but remain to be identified; other methylated derivatives of *d*-galactose may also be present.

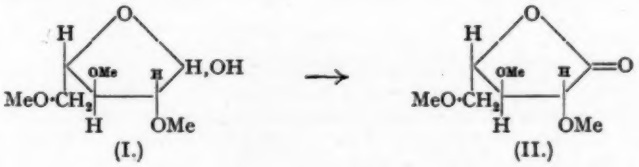
The results indicate the main structural features of the polysaccharide, but owing to the difficulty encountered in effecting the quantitative separation of these sugars it is not possible at this stage to suggest a unique structural formula.

It has been shown (Jones, *J.*, 1939, 558) that cherry gum contains the following sugars in the approximate proportions indicated: *d*-glucuronic acid (1 part), *d*-mannose (1 part), *d*-galactose (2 parts), *l*-arabinose (6 parts), and *d*-xylose (*ca.* 1·5%). The polysaccharide has now been converted into the fully methylated derivative by the thallium hydroxide method of methylation (Menzies, *J.*, 1926, 937; Hirst and Jones, *J.*, 1938, 502). This product is substantially homogeneous since no portions differing materially one from another were obtained on fractionation.

Methylated cherry gum, like methylated damson gum, readily underwent partial methanolysis with methyl alcoholic hydrogen chloride (2%) but there remained a resistant residue which required further prolonged boiling with this reagent before the reaction was complete. Six different sugars were recognised after fractional distillation of the methanolysis products, namely: 2 : 3 : 5-trimethyl *l*-arabinose, 2 : 5-dimethyl *l*-arabinose, 2 : 4 : 6-trimethyl *d*-galactose, 2 : 4-dimethyl *d*-galactose, 2 : 3 : 4-trimethyl *d*-glucuronic acid, and 2 : 3-dimethyl *d*-glucuronic acid. Derivatives of *d*-mannose and of *d*-xylose must be present, but their isolation has not yet been accomplished. It is possible that other methylated galactoses may also be present amonst the products of hydrolysis.

Proof of the identity of these sugar derivatives was obtained as follows:

(*a*) 2 : 3 : 5-Trimethyl *l*-arabinose (I) was identified after oxidation as crystalline 2 : 3 : 5-trimethyl *l*-arabonolactone (II).



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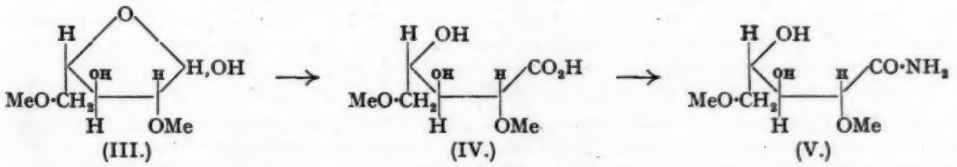
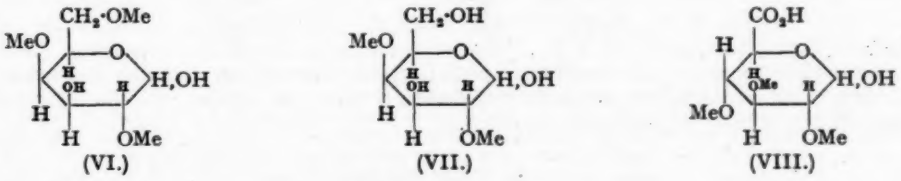


(III.) (IV.) (V.)



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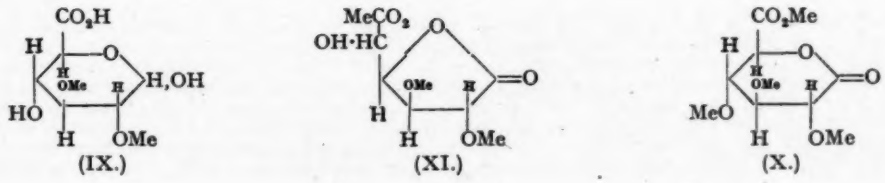


(IX.) (XI.) (X.)

(*b*) 2 : 5-Dimethyl *l*-arabinose (III) was recognised after oxidation as the crystalline lactone and amide (V) of 2 : 5-dimethyl *l*-arabonic acid (IV) (Smith, *J.*, 1940, 1035).

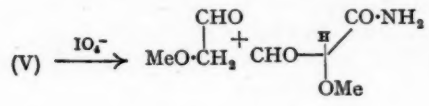
(*c*) 2 : 4 : 6-Trimethyl *d*-galactose (VI) was converted into its characteristic crystalline anilide (Bell and Wilson, *J.*, 1938, 1196; Percival and Somerville, *J.*, 1937, 1615).

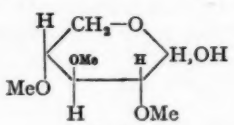
(*d*) 2 : 4-Dimethyl *d*-galactose was isolated as crystalline 2 : 4-dimethyl *d*-galactose (VII) and its crystalline anilide (Smith, *J.*, 1940, 1050).

(*e*) 2 : 3 : 4-Trimethyl (VIII) and 2 : 3-dimethyl *d*-glucuronic (IX) acids were recognised as the corresponding crystalline derivatives of saccharic acid, *viz.* methyl 2 : 3 : 4-trimethyl *d*-saccharolactone ester (X) and methyl 2 : 3-dimethyl *d*-saccharolactone ester (XI).

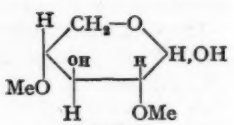
Owing to the difficulty in identifying and separating quantitatively the various glycosides it is not possible to give a precise quantitative estimate of the various sugar derivatives formed on hydrolysis of the methylated polysaccharide. Hence no attempt is made to give a unique formula for cherry gum at this stage. However, a semi-quantitative examination of various sugar residues identified indicates that the ratio of trimethyl *l*-arabofuranose to 2 : 5-dimethyl *l*-arabinose is about 1 : 1 and that the ratio of 2 : 4 : 6-trimethyl *d*-galactose to 2 : 4-dimethyl *d*-galactose is also about 1 : 1.

An inspection of the constants for the pentose fractions shows that derivatives other than 2 : 3 : 5-trimethyl *l*-arabinose and 2 : 5-dimethyl *l*-arabinose must be present in them since both the free sugars and the lactones derived from the pentose fractions had optical rotations too high in the positive sense. 2 : 5-Dimethyl *l*-arabonic acid (IV) and its amide (V) possess hydroxyl groups on adjacent carbon atoms (C_3 and C_4) and should be oxidised by salts of periodic acid. Accordingly, fractions 23, 24, and 25 (see experimental section) were oxidised with periodic acid. From the product a lactone was obtained which must have possessed no α-glycol grouping, and since this lactone behaved as a pyranolactone it must be a derivative of 2 : 4-dimethyl (XIII) or 2 : 3 : 4-trimethyl *d*-xylose (XII) or 2 : 4 : 6-trimethyl *d*-galactose (VI). A pyranose derivative of *l*-arabinose is ruled out as it is known that all the arabinose units are in the furanose form (Jones, *loc. cit.*).





(XII.)



(XIII.)

It has already been shown that 2-(*d*-glucuronosido)-*d*-mannose is part of both the damson gum and cherry gum molecules (Hirst and Jones, *J.*, 1938, 1174), and it is now obvious that both polysaccharides possess other points of similarity. For example, *d*-galactose units which are linked through positions C_3 and C_1 and C_6, C_3, and C_1 occur in both; in addition both molecules contain terminal *l*-arabinose and *d*-glucuronic acid units, and a *d*-glucuronic acid residue linked through C_1 and C_4 is common to both gums. A point of difference, however, is that in cherry gum *l*-arabinose residues occur which are linked through C_1 and C_3 (cf. gum arabic, Smith, *J.*, 1940, 1035) whilst in damson gum the linkage is through C_1 and C_5.

It seems that cherry gum is built up on the same lines as damson gum (Hirst and Jones, *loc. cit.*) and gum arabic (Smith, *loc. cit.*) with probably a main chain of *d*-galactose units to which are attached side chains of aldobionic acids and pentose residues.

A complication arises from the fact that cherry trees may be grown as grafts on different stocks and it remains to be decided whether or not the chemical nature of the exuded gum is dependent upon the type of stock (private communication from F. W. Sansome). Although all the samples of cherry gum which have been examined possess very similar properties, until these points are investigated it cannot be claimed that the results now brought forward necessarily apply to all varieties of cherry gum.

Experimental.

Methylation.—The cherry gum (of English origin) had equiv. 1503, furfuraldehyde 31·8%, and $[\alpha]_D$ −28°. It appeared to be identical with cherry gum obtained from the South of France which had equiv. 1487, furfuraldehyde 31·9%, and $[\alpha]_D$ − 28° (mean values of determinations on seven separate nodules of gum). These figures are closely similar to those given in the literature for other samples of cherry gum isolated from widely different sources. Purified cherry gum (50 g.) (Jones, *J.*, 1939, 558) was dissolved in water (300 c.c.) containing a little N-thallous hydroxide, and a hot concentrated solution of thallous hydroxide (300 c.c. of 4N) was added with stirring. The precipitated thallium complex was rapidly filtered off, washed with methyl alcohol, and dried in a vacuum at 40°. The powdered thallium

derivative (120 mesh) was stirred with methyl iodide, with the exclusion of light and moisture, until the initial reaction had subsided, and the mixture was then boiled (under reflux) until the solid no longer gave an alkaline reaction (50 hours). Excess of methyl iodide was boiled off, the residue was exhaustively extracted with methyl alcohol, and the extracts were concentrated to a cream coloured solid (52 g.). This partly methylated derivative was dissolved in alcohol, and N-thallous ethoxide in benzene (300 c.c.) was added and the mixture evaporated to dryness with the exclusion of carbon dioxide. The solid was powdered (120 mesh), and boiled with methyl iodide until it no longer gave an alkaline reaction to litmus paper. The methylated product was extracted (as above) and the process of methylation with thallous ethoxide twice repeated. A final methylation with Purdie's reagents gave methylated cherry gum (48·0 g.); $[\alpha]_D^{20°}$ − 28° (*c*, 2·1 in methyl alcohol) (Found: equiv., 1650; OMe, 40·7%). This material (42 g.) was submitted to fractionation by precipitation from chloroform solution by addition of light petroleum. Three fractions were obtained as cream coloured solids, soluble in methyl alcohol, benzene, chloroform, acetone, dioxan, and cold water, insoluble in hot water and light petroleum. *Fraction R* (3·0 g.), $[\alpha]_D^{20°}$ − 30° (*c*, 1·4 in methyl alcohol) (Found: uronic anhydride (by boiling with 12% hydrochloric acid under the standard conditions), 10·1%; equiv. (by titration with 0·1N-sodium hydroxide), 1645; OMe, 39·0%). *Fraction S* (37·1 g.), $[\alpha]_D^{20°}$ − 27° (*c*, 2·4 in methyl alcohol) (Found: uronic anhydride, 10·4%; equiv., 1650; OMe, 42·4%). *Fraction T* (1·5 g.), $[\alpha]_D^{20°}$ − 28° (*c*, 0·9 in methyl alcohol) (Found: uronic anhydride, 10·3%; equiv., 1660; OMe, 40·1%. Calc. for fully methylated cherry gum: uronic anhydride, 10·1%; equiv. 1742; OMe, 42·7%).

Hydrolysis.—The methylated gum (Fraction S, 30 g.) was dissolved in 2% methyl alcoholic hydrogen chloride (300 c.c.) and boiled under reflux for 70 hours by which time $[\alpha]_D$ had changed from −27° to + 14°. The cooled solution was neutralised with silver carbonate, filtered, and evaporated to a syrup (34·4 g.), part of which was soluble in ether (A, 27·3 g., $n_D^{19°}$ 1·4545) and part insoluble (B, 7·1 g., $n_D^{19°}$ 1·4810).

The ether-soluble syrup (A, 27·3 g.) was heated to 90° with 0·3N-barium hydroxide (70 c.c.) for 15 hours, cooled, neutralised with carbon dioxide, and filtered, and the filtrate exhaustively extracted with chloroform in an all-glass apparatus. The chloroform extracts were evaporated to a syrup, $n_D^{20°}$ 1·4492, which on extraction with boiling ether gave a fraction soluble in ether (C, 17·45 g., $n_D^{21°}$ 1·4453) and an insoluble residue (D, 3·80 g., $n_D^{21°}$ 1·4624). The aqueous solution of the chloroform extraction was evaporated at 40°/12 mm. to a brown solid (E, 6·4 g.).

Fraction C (17·45 g.) was fractionally distilled in a vacuum, giving: *Fraction* (1), 2 : 3 : 5-trimethyl methyl-*l*-arabofuranoside (7·80 g.), b. p. 110—120°/0·001 mm. (bath temp.), $n_D^{19°}$ 1·4380 (Found: OMe, 60·5%). *Fraction* (2), a mixture of 2 : 3 : 5-trimethyl methyl-*l*-arabofuranoside and 2 : 5-dimethyl methyl-*l*-arabofuranoside (2·11 g.), b. p. 120°/0·001 mm. (bath temp.), $n_D^{19°}$ 1·4438 (Found: OMe, 58·3%). *Fraction* (3), mainly 2 : 5-dimethyl methyl-*l*-arabofuranoside (5·14 g.), b. p. 125—140°/0·001 mm. (bath temp.), $n_D^{20°}$ 1·4532 (Found: OMe, 51·0%).

To the still residue was added fraction D (3·80 g.) and the distillation continued. *Fraction* (4), mainly 2 : 4 : 6-trimethyl methyl-*d*-galactoside (2·66 g.), b. p. 140—150°/0·001 mm. (bath temp.), $n_D^{19°}$ 1·4560 (Found: OMe, 50·4%). *Fraction* (5), 2 : 4 : 6-trimethyl methyl-*d*-galactoside (0·85 g.), b. p. 150—160°/0·001 mm. (bath temp.), $n_D^{20°}$ 1·4618 (Found: OMe, 50·4%). This fraction partially crystallised. Still residue (F).

The ether-insoluble syrup B (7·1 g.) and the solid residue E (6·4 g.) were united and boiled with 2% methyl-alcoholic hydrogen chloride (300 c.c.) for 72 hours. The solution was neutralised with silver carbonate, filtered, and concentrated to a syrup which was heated with 0·3N-barium hydroxide (90 c.c.) for 12 hours. The cooled solution was neutralised with carbon dioxide, filtered, and exhaustively extracted with chloroform, and the extracts were concentrated to a syrup (G, 4·78 g., $n_D^{18°}$ 1·4730), which was added to the still residue (F) and the fractionation continued, giving: *Fraction* (6), mainly 2 : 3 : 5-trimethyl methyl-*l*-arabofuranoside (1·278 g.), b. p. 110°/0·001 mm. (bath temp.), $n_D^{19°}$ 1·4372 (Found: OMe, 58·0%). *Fraction* (7), a mixture of 2 : 5-dimethyl methyl-*l*-arabofuranoside and 2 : 4 : 6-trimethyl methyl-*d*-galactoside (0·70 g.), b. p. 120—150°/0·001 mm. (bath temp.), $n_D^{19°}$ 1·4572 (Found: OMe, 52·3%). *Fraction* (8), mainly 2 : 4-dimethyl methyl-*d*-galactoside (4·25 g.), b. p. 160°/0·001 mm. (bath temp.), $n_D^{20°}$ 1·4750 (Found: OMe, 38·4%). *Fraction* (9), dimethyl and monomethyl methyl-hexosides (1·15 g.), b. p. 160—200°/0·001 mm. (bath temp.), $n_D^{18°}$ 1·4845 (Found: OMe, 31·7%). Still residue, (0·38 g.).

The aqueous solution from G was evaporated to dryness and the residual barium salts were boiled with 6% methyl alcoholic hydrogen chloride (200 c.c.) for 24 hours. The solution was neutralised with barium carbonate, filtered, and evaporated to a syrupy mass which was exhaustively extracted with acetone. Removal of the solvent at 40°/12 mm. gave a syrup ($n_D^{21°}$ 1·4722), part of which (3·80 g.) was separated into two fractions by extraction with ether. The ether-soluble material (2·90 g., $n_D^{20°}$ 1·4625) was fractionally distilled in a vacuum, giving: *Fraction* (10), mainly the methyl ester of 2 : 3 : 4-trimethyl methyl-*d*-glucuronoside (1·63 g.), b. p. 120°/0·001 mm. (bath temp.), $n_D^{18·5°}$ 1·4530 (Found: OMe, 55%). This fraction was partially crystalline. *Fraction* (11), mainly the methyl ester of dimethyl methylglucuronoside (0·83 g.), b. p. 150°/0·001 mm. (bath temp.), $n_D^{18°}$ 1·4681 (Found: OMe, 48·7%). To the still residue was added the ether-insoluble portion (0·90 g.) of the glucuronic acid fractions and the distillation was continued, giving: *Fraction* (12), a mixture of the methyl esters of 2 : 3 : 4-trimethyl methyl-*d*-glucuronoside and dimethyl methyl-*d*-glucuronoside (0·60 g.), b. p. 160—200°/0·001 mm. (bath temp.), $n_D^{19°}$ 1·4698 (Found: OMe, 48·8%).

Examination of the Various Fractions.—Fractions (1), (2), and (6) were combined (11·1 g.) and hydrolysed with 0·1N-sulphuric acid (90 c.c.) for 7½ hours at 90°. $[\alpha]_D^{20°}$ − 20° (*c*, 11·1 in 0·1N-sulphuric acid, initial value); − 20° (1½ hours); − 10° (3½ hours); ±0° (7½ hours, constant value). The solution was neutralised with barium carbonate, filtered, and evaporated to a syrup at 40°/12 mm., and the sugars were exhaustively extracted with chloroform. Concentration of the extracts gave a syrup (9·28 g., $n_D^{18°}$ 1·4522), a portion (8·68 g.) of which was fractionally distilled in a vacuum giving: *Fraction* (13) (7·40 g.), 2 : 3 : 5-trimethyl *l*-arabofuranose, b. p. 108—120°/0·001 mm. (bath temp.), $n_D^{21°}$ 1·4540; $[\alpha]_D^{20°}$ ±0° (*c*, 0·9 in water) (Found: OMe, 48·0. Calc. for $C_8H_{16}O_5$: OMe, 48·4%).

Fraction (14) (0·83 g.), b. p. 120—140°/0·001 mm. (bath temp.), [$n_D^{19°}$] 1·4668, [α]$_D^{20°}$ + 47° (*c*, 0·55 in water) (Found: OMe, 42·8%). *Residue* (0·25 g.).

Fraction (13) (6·80 g.) was dissolved in water (20 c.c.) and oxidised with bromine (5 c.c.). The lactones (6·40 g.; $n_D^{17°}$ 1·4538) isolated in the usual manner were fractionally distilled giving *Fraction* (15), mainly 2 : 3 : 5-trimethyl *l*-arabonolactone (2·5 g.), b. p. 104°/0·001 mm. (bath temp.), $n_D^{18°}$ 1·4452 (supercooled liquid), m. p. and mixed m. p. with an authentic specimen 27°, [α]$_D^{20°}$ − 28° (initial value in water; *c*, 1·58); − 29° (2 hours); − 32° (4¼ hours); − 35° (6¾ hours); − 33° (22 hours); − 32° (29½ hours); − 31° (49 hours) (Found: equiv., 198; OMe, 48·3%). With liquid ammonia the lactone gave in good yield 2 : 3 : 5-trimethyl *l*-arabonamide, m. p. and mixed m. p., 138°. *Fraction* (16) (1·93 g.), mainly 2 : 3 : 5-trimethyl *l*-arabonolactone, b. p. 104—124°/0·001 mm. (bath temp.), $n_D^{18°}$ 1·4500. [α]$_D^{20°}$ + 8° (*c*, 1·8 in water, initial value); − 2° (1 hour); − 17° (4 hours); − 19° (6 hours); − 26° (22 hours); − 25° (33 hours); − 24° (49 hours) (Found: equiv., 198; OMe, 51·0%). With liquid ammonia this lactone gave 2 : 3 : 5-trimethyl *l*-arabonamide, m. p. 138° in 70% yield. Fractions (15) and (16) were both contaminated with a lactone which, from its rate of mutarotation, was a δ-lactone and which may have been a derivative of *d*-xylonic or *d*-galactonic acid. The residue (2·0 g.) is considered below.

Fractions (3), (4), and (7) were combined (8·40 g.) and hydrolysed with N-sulphuric acid (100 c.c.) during 7 hours at 90°. [α]$_D^{20°}$ + 21° (initial value); + 55° (¾ hour); + 56° (1½ hours); + 54° (2½ hours); + 52° (4 hours); + 48° (7 hours, constant value). The solution was neutralised with barium carbonate, filtered, and evaporated, and the residual syrupy sugars (7·64 g., $n_D^{17°}$ 1·4740) were isolated in the usual manner and distilled, giving: *Fraction* (17) (2·29 g.), mainly 2 : 5-dimethyl *l*-arabinose, b. p. 128—133°/0·001 mm. (bath temp.), $n_D^{20°}$ 1·4668. [α]$_D^{22°}$ + 60° (*c*, 0·96 in water) (Found: OMe, 41·4%). *Fraction* (18) (3·36 g.), b. p. 135°/0·001 mm. (bath temp.), $n_D^{15°}$ 1·4735. [α]$_D^{22°}$ + 36° (*c*, 1·6 in water) (Found: OMe, 42·0%). *Fraction* (19) (1·07 g.), b. p. 140—170°/0·001 mm. (bath temp.). [α]$_D^{20°}$ + 39° (*c*, 0·88 in water) (Found: OMe, 36·9%). *Residue* (0·73 g.).

Fractions (14), (17), (18), and (19) were combined (7·4 g.) and oxidised with bromine water. The lactones (6·60 g.) were isolated, combined with the residue (2·0 g.) from fractions (15) and (16), and fractionally distilled in a vacuum giving *Fraction* (20) (1·15 g.), 2 : 5-dimethyl *l*-arabonolactone admixed with some other lactone of higher positive rotation (2 : 4 : 6-trimethyl *d*-galactonolactone?), b. p. 130—140°/0·001 mm. (bath temp.), $n_D^{18°}$ 1·4562. [α]$_D^{20°}$ + 14° (*c*, 1·25 in water, initial value); + 4° (1¾ hours); − 12° (5¾ hours); − 16° (9 hours); − 15° (22 hours) (Found: equiv., 187; OMe, 38·8%. Calc. for $C_7H_{12}O_6$: equiv., 176; OMe, 35·2%). With liquid ammonia the lactone gave 2 : 5-dimethyl *l*-arabonamide in good yield, m. p. and mixed m. p. with an authentic specimen, 131° (Smith, *J.*, 1939, 751) depressed to 122° on admixture with 2 : 3-dimethyl *l*-arabonamide. 2 : 5-Dimethyl *l*-arabonamide gave a negative Weerman test.

Conversion of 2 : 5-*Dimethyl* l-*Arabonamide into* 2 : 5-*Dimethyl* l-*Arabonolactone*.—The amide (0·4 g.) was heated at 90° with excess of N-sodium hydroxide until ammonia was no longer evolved (2 hours). The solution was acidified with N-sulphuric acid and then extracted exhaustively with chloroform. Concentration of the chloroform solution gave a syrup (0·35 g.) which was distilled in a vacuum; b. p. 160°/0·3 mm. The product crystallised, had m. p. 60°, and was pure 2 : 5-dimethyl *l*-arabonolactone (Found: OMe, 35·0. Calc. for $C_7H_{12}O_5$: OMe, 35%). *Fraction* (21) (5·09 g.) was mainly 2 : 5-dimethyl *l*-arabonolactone, b. p. 150°/0·001 mm. (bath temp.), $n_D^{19°}$ 1·4642. [α]$_D^{20°}$ + 21° (*c*, 1·97 in water, initial value); + 8° (1¾ hours); − 8° (5¾ hours); − 11° (9 hours); − 11° (22 hours); − 10° (38 hours) (Found: equiv., 189; OMe, 35·3%). With liquid ammonia the lactone gave 2 : 5-dimethyl *l*-arabonamide, m. p. 131°, in 60% yield. *Fraction* (22) (1·50 g.), had b. p. 160—180°/0·001 mm. (bath temp.), $n_D^{19°}$ 1·4720 (Found: OMe, 32·8%), and gave no crystalline amide with liquid ammonia.

The non-crystalline amides from Fractions (15) and (16) were combined and heated with barium hydroxide in a stream of nitrogen until the solution was free from ammonia. Excess of barium hydroxide was removed by carbon dioxide and the filtered solution decomposed with the calculated quantity of N-sulphuric acid, filtered, and evaporated to a syrup. In a similar manner lactones were regenerated from fractions (20), (21), and (22). The lactones recovered from (15) and (16) were distilled in a vacuum, giving *Fraction* (23), b. p. 120°/0·001 mm. (bath temp.), $n_D^{19°}$ 1·4550. [α]$_D^{20°}$ + 33° (*c*, 0·84 in water); + 27° (1 hour); + 14° (2 hours); + 7° (3½ hours); − 5° (7 hours); − 11° (11 hours); − 11° (23 hours). (Found: equiv., 200; OMe, 46·4%). With liquid ammonia the lactone gave an amide from which a small amount (50 mg.) of 2 : 3 : 5-trimethyl *l*-arabonamide was isolated; m. p. 138°. The syrupy amide gave a negative Weerman reaction showing the absence of amides with hydroxyl groups on C_2. The lactones from Fractions (20), (21), and (22) were fractionally distilled in a vacuum, giving: *Fraction* (24), b. p. 160°/0·001 mm. (bath temp.), $n_D^{19°}$ 1·4648. [α]$_D^{20°}$ + 43° (*c*, 2·35 in water; initial value); + 32° (1 hour); + 18° (2 hours); + 8° (3½ hours); − 4° (7 hours); − 10° (22 hours) (Found: equiv., 184; OMe, 39·5%). With liquid ammonia this lactone gave a syrupy amide which gave a negative Weerman test. *Fraction* (25), b. p. 160—170°/0·001 mm., $n_D^{19°}$ 1·4740. [α]$_D^{20°}$ + 14° (*c*, 0·85 in water, initial value); + 8° (1½ hours); + 0° (2¾ hours); − 6° (12¾ hours); − 11° (25 hours); − 7° (31¾ hours) (Found: equiv., 186; OMe, 36·4%). This lactone reacted with liquid ammonia giving a syrupy amide which gave a positive Weerman reaction.

The non-crystalline amides (3·50 g.) from the above lactones [Fractions (23), (24), and (25)] were dissolved in water and excess of periodic acid added. The solution become hot, and an odour resembling that of acetaldehyde was detected; this reaction destroyed all the 2 : 5-dimethyl *l*-arabonamide present in the syrupy amides. The solution was neutralised with barium carbonate and filtered, and the filtrate concentrated at 40°/12 mm. The distillate had an aldehydic odour and reduced hot Fehling's solution. The residual syrup was dissolved in water and oxidised with bromine in the presence of barium carbonate until non-reducing to Fehling's solution. Bromine was removed by aeration, the filtered solution evaporated to dryness, and the residue boiled with 2% methyl alcoholic hydrogen chloride for 10 hours. Hydrochloric acid was removed with silver carbonate, and the filtered solution evaporated at 90°/760 mm., to a syrup which was distilled in a vacuum, giving: *Fraction* (26) (1·8 g.), b. p. 135—145°/0·001 mm. (bath temp.), $n_D^{22°}$ 1·4538. [α]$_D^{20°}$ + 50° (*c*, 1·2 in water, initial

value); + 40° (1½ hours); + 23° (4 hours); + 15° (7 hours); + 11° (23 hours); + 11° (28 hours, constant value) (Found: equiv., 175; OMe, 47·9%). With liquid ammonia the distilled lactone gave no crystalline amide. As no dimethyl dimethoxysuccinate was isolated, it is inferred that 2 : 3-dimethyl arabinose and 2 : 3-dimethyl xylose are not present in Fractions (23), (24), and (25). *Fraction* (27) (0·8 g.), b. p. 145—165°/0·001 mm. (bath temp.), $n_D^{21°}$ 1·4628. $[\alpha]_D^{20°}$ + 77° (*c*, 1·0 in water, initial value); + 59° (2 hours); + 33° (5¾ hours); + 23° (24 hours, constant value) (Found: equiv., 190; OMe, 45·7%). This fraction gave no crystalline derivative on conversion into the corresponding amide by solution in liquid ammonia. This amide and the amide from Fraction (26) gave no sodium cyanate with sodium hypochlorite, proving the absence of a hydroxyl group on C_3. 3 : 4-Dimethyl arabinose, 3 : 4-dimethyl xylose, and 3 : 4 : 6-trimethyl *d*-mannose are thus absent from this fraction.

Fraction (5) (0·82 g.) was dissolved in N-hydrochloric acid (20 c.c.) and heated at 90—95° for 3 hours. $[\alpha]_D^{20°}$ + 90° (initial value); + 77° (1 hour); + 69° (2¾ hours, constant value). The solution was neutralised with silver carbonate, filtered and evaporated to a syrup (0·80 g.), $n_D^{20°}$ 1·4738. $[\alpha]_D^{20°}$ + 75° (*c*, 4·0 in water) (Found: OMe, 39·0%). The syrup (0·79 g.) on being refluxed with alcoholic aniline gave 2 : 4 : 6-trimethyl *d*-galactose anilide (0·47 g.), m. p. and mixed m. p. 179°. The non-crystalline anilide was heated with N-hydrochloric acid (10 c.c.) at 70° for 3 hours. The cooled solution was neutralised with silver carbonate, filtered, and exhaustively extracted with light petroleum, and the extracted solution evaporated to a syrup which did not crystallise. The recovered sugar was oxidised with bromine water and the lactone isolated as a syrup which gave with liquid ammonia a non-crystalline amide. The amide gave no sodium cyanate with sodium hypochlorite (Weerman reaction), proving the absence of a hydroxyl group on C_2 and therefore of a mannose derivative in this fraction (see Jones, *loc. cit.*). The yield of 2 : 4 : 6-trimethyl *d*-galactose anilide corresponds to the presence of 0·50 g. of 2 : 4 : 6-trimethyl *d*-galactose in this fraction.

Fraction (8) (4·19 g.) was dissolved in N-hydrochloric acid (50 c.c.) and heated at 90—95° for 4 hours. $[\alpha]_D^{20°}$ + 74° (initial value), rising to + 78° (constant value). The solution was neutralised with silver carbonate, filtered, and evaporated to a syrup (3·98 g.) which did not crystallise and had $[\alpha]_D^{20°}$ + 85° (in water) (Found: OMe, 25·2%). The sugar (3·50 g.) on being heated with alcoholic aniline gave 2 : 4-dimethyl *d*-galactose anilide (0·62 g.), m. p. and mixed m. p. with an authentic specimen 212°, and a syrupy anilide (Y). This corresponds to the presence of 1·08 g. of 2 : 4-dimethyl *d*-galactose in this fraction. The crystalline anilide was hydrolysed with N-hydrochloric acid at 90° for 2 hours, the cooled solution neutralised with silver carbonate, and filtered, aniline extracted with ether, and the aqueous solution evaporated to a syrup which crystallised on nucleation with the monohydrate of 2 : 4-dimethyl *d*-galactose; m. p. and mixed m. p. with an authentic specimen 105°. The sugar (0·30 g.) was oxidised with bromine water and the lactone of 2 : 4-dimethyl *d*-galactonic acid (0·20 g.) isolated as a syrup, $[\alpha]_D^{20°}$ + 100° ⟶ + 40° (60 hours, constant value), which on solution in liquid ammonia gave 2 : 4-dimethyl *d*-galactonamide (0·11 g.). $[\alpha]_D^{20°}$ + 58° (*c*, 1·1 in water); m. p. and mixed m. p. 164° (Found: OMe, 27·6. Calc. for $C_8H_{17}O_6N$: OMe, 27·8%).

The filtrate from the anilide (Y) was evaporated to a syrup and hydrolysed with N-hydrochloric acid, and the free sugar (2·35 g., $n_D^{22°}$ 1·4842) isolated in the usual manner. The sugar was boiled in 2% methyl alcoholic hydrogen chloride and the resulting glycosides isolated and distilled; b. p. 160—180°/0·002 mm. (bath temp.), $n_D^{18·5°}$ 1·4700 (Found: OMe, 41·7%). This substance which analysed as a dimethyl methylhexoside failed to give any crystalline products on hydrolysis.

Fraction (9) (0·91 g.) was hydrolysed with N-hydrochloric acid (30 c.c.) for six hours at 95°. $[\alpha]_D^{20°}$ + 60° ⟶ + 85° (constant value). The sugars (0·7 g.) isolated in the usual manner did not crystallise and no crystalline derivative could be isolated from them.

Fraction (10) (1·3 g.) was hydrolysed with boiling N-hydrochloric acid and the resultant 2 : 3 : 4-trimethyl *d*-glucuronic acid isolated. It was converted by oxidation with bromine water into 2 : 3 : 4-trimethyl *d*-saccharic acid which was isolated as follows. Bromine was removed mainly by aeration, the last traces being removed by the passage of sulphur dioxide. The solution containing the methylated derivative was then extracted exhaustively with chloroform and the extracts were concentrated to a syrup (1·1 g.) which was esterified by boiling with methyl alcoholic hydrogen chloride. The resultant dimethyl ester of 2 : 3 : 4-trimethyl *d*-saccharic acid was isolated and converted into the methyl ester of 2 : 3 : 4-trimethyl saccharolactone by distillation in a vacuum. The product (0·9 g.), $n_D^{20°}$ 1·4605, crystallised and was purified by recrystallisation from ether; m. p. and mixed m. p. with an authentic specimen 110°.

Fractions (11) and (12) were combined and a portion of the mixture (0·9 g.) was hydrolysed. The resultant mixture of 2 : 3 : 4-trimethyl *d*-glucuronic acid and 2 : 3-dimethyl *d*-glucuronic acid was oxidised and the product converted into the corresponding dimethyl esters of 2 : 3 : 4-trimethyl and 2 : 3-dimethyl *d*-saccharic acid as described above. Distillation of this mixture (0·6 g.) gave a fraction (0·2 g.), b. p. 140°/0·0 mm., $n_D^{20°}$ 1·4650, which crystallised in part and from which methyl 2 : 3 : 4-trimethyl *d*-saccharolactone, m. p. 110°, was obtained by tiling the crystals followed by recrystallisation of the product from ether. A higher boiling fraction (0·3 g.), up to 200°/0·01 mm., $n_D^{20°}$ 1·4730, crystallised on nucleation with methyl 2 : 3-dimethyl *d*-saccharolactone. The crystals were separated by tiling and were purified by recrystallisation from alcohol–ether; m. p. 101°—not depressed on admixture with an authentic specimen.

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199. *Some Reactions and Derivatives of* 6- *and* 7-*Nitro*-2-*naphthylamines. Part II. Nitration and Diazo-coupling.*

By Herbert H. Hodgson and Edward R. Ward.

The acetyl and toluene-*p*-sulphonyl derivatives of 6- and 7-nitro-2-naphthylamines nitrate in the 1-position, and the dinitro-compounds are highly resistant to further nitration. 6- and 7-Nitro-2-naphthylamines couple in the 1-position, and the resulting *o*-aminoazo-compounds are oxidised to triazoles. Replacement of the amino- by the acetoxy-group in 6- and 7-nitro-*p*-nitrobenzeneazo-2-naphthylamines readily occurs by heating in glacial acetic acid with sodium nitrite.

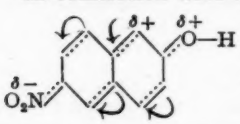
Further nitration of both the acetyl and the toluene-*p*-sulphonyl derivatives of 6- and 7-nitro-2-naphthylamines occurs in the 1-position only, and absence of nitration in the 3-position, as pointed out by Bell (*J.*, 1929, 2784) for the corresponding derivatives of β-naphthylamine, is now further emphasised.

It may be noted that the further nitration of six of the eight possible heteronuclear mononitrotoluene-*p*-sulphon-naphthalides has now been investigated, and whereas the four heteronuclear mononitro-2-naphthalides are only mononitrated in acetic acid medium with fuming nitric acid, both 5- and 6-nitro-1-naphthalides are simultaneously dinitrated. This is in contrast to the simultaneous dinitration of the unsubstituted 1- and 2-toluene-*p*-sulphonnaphthalides. Incidentally, however, the *m*-nitrobenzenesulphonyl derivatives of 8-nitro- and 1 : 6-dinitro-2-naphthylamines both afforded the 1 : 6 : 8-trinitro-derivative on further nitration (Bell, *loc. cit.*).

The constitutions of the 1 : 7-*dinitroaceto*- and 1 : 7-*dinitrotoluene*-p-*sulphon*-2-*naphthalides* were established by hydrolysis to the amine followed by its diazotisation and deamination to the known 1 : 7-dinitronaphthalene (cf. Hodgson and Birtwell, *J.*, 1943, 433).

6- and 7-Nitro-2-naphthylamines, used as second components, both couple in alcoholic acetic acid with diazotised amines in the 1-position as shown by oxidation of the resulting *o*-aminoazo-compounds to triazoles, by their resistance to acetylation, and by their diazotisation and conversion into a mixture of *o*-azonaphthol and *o*-azonaphthyl acetate by the sodium nitrite–glacial acetic procedure of Hodgson and Foster (*J.*, 1942, 435) [cf. also Morgan and Chazan (*J. Soc. Chem. Ind.*, 1922, **41**, 1T) and Morgan and Gilmour (*ibid.*, p. 61T) who showed similarly that 5- and 8-nitro-2-naphthylamines coupled in the 1-position]. 6- and 7-*Nitro*-p-*nitrobenzeneazo*-2-*naphthylamines* behaved somewhat differently towards the Hodgson and Foster procedure (*loc. cit.*), the former being hydrolysed more readily to give predominant naphthol in the mixture of naphthol and naphthyl acetate obtained, whereas the latter afforded a good yield of the 7-*nitro*-1-p-*nitrobenzeneazonaphthyl acetate*. It is noteworthy that tar was absent in these decompositions, indicating ease of replacement of the amine by the acetoxy-group. Previously, Hodgson and Foster (*loc. cit.*) had found, for azo-dyes with unsubstituted β-naphthylamine as second component, that meta-directing groups in the first component promoted this replacement, so that evidence is now to hand of the same effect by the meta-directing 6- and 7-nitro-groups in the β-naphthylamine component.

In connection with the transmissions of effects from the 6- to the 2-position (cf. Robinson and Thompson, *J.*, 1932, 2015), it is of interest that 6-nitro-2-naphthol would not couple with diazotised *p*-nitroaniline in either ethanol or aqueous sodium carbonate solution, showing the deactivating effect of the 6-nitro- on the phenolic group, in the potential ionic quinonoid structure, in which the 1-position, instead of acquiring the anionoid activity requisite for coupling, becomes kationoid.



The claim of Friedländer and Littner (*Ber.*, 1915, **48**, 330) to have prepared some 5-nitro-aceto-2-naphthalide from β-acetonaphthalide, and since disproved by Veselý and Jakeš (*Bull. Soc. chim.*, 1923, **33**, 942), has erroneously been repeated in *Org. Synth.*, 1933, **13**, 73.

Experimental.

Nitration of 7-*Nitro*-2-*acetonaphthalide.*—7-Nitro-2-naphthylamine (3 g.) was refluxed with glacial acetic acid (12 c.c.) and acetic anhydride (3 c.c.) for 10 minutes; on cooling, an almost quantitative separation of 7-nitro-2-acetonaphthalide was obtained, which, after recrystallisation from 50% ethanol, had m. p. 221°. This acetyl compound (3 g.) was added gradually to nitric acid (12 c.c., *d* 1·5) during 15 minutes (the temperature being kept below 20°), and, after being stirred for a further 15 minutes, the mixture was poured on ice and the precipitate of 1 : 7-*dinitro*-2-*acetonaphthalide* (3·5 g.) removed, washed with water, and dried; it crystallised from glacial acetic acid in pale yellow needles, m. p. 222°

(Found: N, 15·1. $C_{11}H_9O_5N_3$ requires N, 15·3%). Should the temperature be allowed to rise during nitration even as high as 60° for 5—10 minutes, some oxidation occurs although the final product is mainly 1 : 7-dinitro-2-acetonaphthalide.

1 : 7-*Dinitro*-2-*naphthylamine* was obtained when the acetyl derivative above (2·5 g.) was hydrolysed by refluxing with a solution of ethanol (25 c.c.) and 50% aqueous sulphuric acid (25 c.c.) for 45 minutes; after cooling, the separated 1 : 7-dinitro-2-naphthylamine (2 g.) was filtered off, washed with ethanol, and dried; it crystallised from 50% aqueous pyridine in golden yellow needles, m. p. 248—249° (Found: N, 18·1. $C_{10}H_7O_4N_3$ requires N, 18·0%). Deamination of the amine (1·5 g.) occurred when its solution below 20° in sulphuric acid (8 c.c., *d* 1·84) containing sodium nitrite (0·6 g.) was stirred gradually into glacial acetic acid (20 c.c.), the stirring continued for 30 minutes, red copper oxide (2—3 g.) added portionwise during 15 minutes, and the temperature allowed to rise to 40°. After being stirred for a further 1 hour, the mixture was poured on ice, the precipitate of 1 : 7-dinitronaphthalene filtered off, washed with water, dried, extracted with boiling ethylene dichloride, the solvent removed from the extract, and the 1 : 7-dinitronaphthalene purified by sublimation at 190—200°/15 mm.; m. p. and mixed m. p. with an authentic specimen, 156° (Veselý and Dvorák, *Bull. Soc. chim.*, 1923, **33**, 319, give m. p. 156°).

Nitration of 7-*Nitrotoluene*-p-*sulphon*-2-*naphthalide*.—A solution of the naphthalide (2·5 g.) in glacial acetic acid (20 c.c.) at 60° was treated first with a crystal of sodium nitrite and then with 7·5 c.c. of a solution made up of nitric acid (1 c.c., *d* 1·5) in glacial acetic acid (9 c.c.); nitration began when the temperature was raised to 65°, and for completion the mixture was kept at 90° for 5 minutes; on cooling, 1 : 7-*dinitro*-p-*toluenesulphon*-2-*naphthalide* (1·7 g.) crystallised out; after removal, it was washed with glacial acetic acid and ether, and dried. It crystallised from glacial acetic acid in bright yellow rectangular plates, m. p. 165—166° (Found: N, 11·0. $C_{17}H_{13}O_6N_3S$ requires N, 10·8%). On hydrolysis by dissolution (1 g.) in sulphuric acid (10 c.c., *d* 1·84) and heating for 5 minutes at 40°, 1 : 7-dinitro-2-naphthylamine was obtained and precipitated by pouring the mixture on ice, with subsequent treatment as above. Alternatively, the 1 : 7-dinitro-*p*-toluenesulphon-2-naphthalide was converted directly into 1 : 7-dinitronaphthalene by the Hodgson and Birtwell procedure (*loc. cit.*), but diazotisation had to be carried out carefully since hydrolysis and diazotisation followed rapidly.

Coupling with Diazo-compounds.—To a solution of the naphthylamine (0·01 g.-mol.) in ethanol (400 c.c.) containing sufficient sodium acetate for the replacement by acetic acid of all mineral acid involved, was added an aqueous solution of the diazonium salt (chloride or sulphate, 0·01 g.-mol.), prepared from *p*-nitroaniline, *p*-chloroaniline, or *p*-toluidine, from which free nitrous acid had been removed by urea. The mixture was stirred for 1 hour, and the azo-dye filtered off, washed with cold ethanol (50 c.c.) and hot water, dried, and crystallised from nitrobenzene (charcoal). All the azo-dyes now described were moderately soluble in boiling acetic anhydride or boiling glacial acetic acid, and resisted acetylation thereby even at 100°; they were only slightly soluble in boiling toluene or ethanol. The sequence of colours produced by concentrated sulphuric acid and subsequent dilution with water are recorded immediately after the m. p. The large amount of ethanol used for the couplings is necessary to prevent uncoupled amine from separating with the azo-dye.

6-*Nitro*-p-*nitrobenzeneazo*-2-*naphthylamine* formed micro-needles, m. p. 304° (sintered at 290°; blood-red, salmon-pink, brownish-red precipitate) (Found: N, 21·1. $C_{16}H_{11}O_6N_5$ requires N, 20·8%). 6-*Nitro*-1-p-*chlorobenzeneazo*-2-*naphthylamine* formed orange-red micro-needles, m. p. 261° (sintered at 245°; magenta, red to yellow-brown) (Found: N, 17·4. $C_{16}H_{11}O_3N_4Cl$ requires N, 17·15%). 6-*Nitro*-1-p-*tolylazo*-2-*naphthylamine* formed orange red micro-plates, m. p. 234° (mauve, magenta, reddish-brown, orange) (Found: N, 18·5. $C_{17}H_{14}O_2N_4$ requires N, 18·3%). 7-*Nitro*-1-p-*chlorobenzeneazo*-2-*naphthylamine* formed felted scarlet needles, m. p. 199° (magenta, purple, brown precipitate) (Found: N, 17·4. $C_{16}H_{11}O_3N_4Cl$ requires N, 17·15%). 7-*Nitro*-1-p-*nitrobenzeneazo*-2-*naphthylamine* formed very dark red almost black needles, m. p. 265—266° (crimson, reddish-blue) (Found: N, 21·1. $C_{16}H_{11}O_6N_5$ requires N, 20·8%).

Oxidation of Azo-dyes to Triazoles.—The dye (0·5 g.) was dissolved in boiling glacial acetic acid (30 c.c.), and a solution of chromium trioxide (0·5 g.) in water (1 c.c.) was added with caution to the stirred boiling mixture; the red colour disappeared, to be replaced by a white precipitate. On cooling and dilution with water, the triazole separated; it was filtered off, washed with hot water until the filtrate was colourless, dried at 100°, and recrystallised from hot nitrobenzene.

6-*Nitro*-1 : 2-*naphtho*-p-*nitrophenyltriazole* crystallised in flesh-coloured micro-plates, m. p. 288° (Found: N, 21·3. $C_{16}H_9O_4N_5$ requires N, 20·9%). 7-*Nitro*-1 : 2-*naphtho*-p-*nitrophenyltriazole* crystallised in flesh-coloured plates, m. p. 311—312° (sintered at 300°) (Found: N, 21·3. $C_{16}H_9O_4N_5$ requires N, 20·9%).

Reactions of 6- *and* 7-*Nitro*-1-p-*nitrobenzeneazo*-2-*naphthylamines with Sodium Nitrite in Glacial Acetic Acid*.—(*a*) The 6-nitro-compound (1·0 g.) was dissolved in hot glacial acetic acid (350 c.c.) at 70°, and treated portionwise with finely powdered sodium nitrite (1 g.); nitrogen was briskly evolved, and, when the evolution had ceased, the solution was raised to the boil for 15 minutes. On cooling, no separation occurred, so water was added to precipitate the reaction product which was a mixture of difficultly separable 6-nitro-1-*p*-nitrobenzeneazo-2-naphthol and its acetate. When the precipitate (0·25 g.) was refluxed with ethanol (50 c.c.) containing hydrochloric acid (2 c.c., *d* 1·18) for 30 minutes, complete hydrolysis occurred, and the 6-*nitro*-1-p-*nitrobenzeneazo*-2-*naphthol* separated on cooling and was removed, washed, and dried; it crystallised from boiling glacial acetic acid in pillar-box red microcrystals, m. p. 314° (sintered at 305°; reddish salmon pink, orange-red) (Found: N, 16·7. $C_{16}H_{10}O_5N_4$ requires N, 16·5%), which were only slightly soluble in hot glacial acetic acid, almost insoluble in boiling ethanol, and readily soluble in boiling nitrobenzene. Alternatively, the dye (0·5 g.) was added gradually to a solution of sodium nitrite (0·15 g.) in sulphuric acid (4 c.c., *d* 1·84) at 0°, followed by the gradual addition of glacial acetic acid (5 c.c.) over 15 minutes below 20°. After a further 15 minutes ice chips were added and stirring maintained until evolution of nitrogen had ceased; on dilution with water 6-nitro-1-*p*-nitrobenzeneazo-2-naphthol separated.

(*b*) The 7-nitro-compound (1 g.) was dissolved in glacial acetic acid (200 c.c.), in which it is more soluble than the 6-nitro-isomeride, and treated as above so far as the boiling operation, when on cooling

there separated *7-nitro*-1-p-*nitrobenzeneazo*-2-*naphthyl acetate*, which crystallised from boiling acetic acid in orange red needles, m. p. 233° (red violet, orange) (Found N, 15·0. $C_{16}H_{12}O_6N_4$ requires N, 14·7%). *7-Nitro*-1-p-*nitrobenzeneazo*-2-*naphthol* was obtained by hydrolysis as above, and crystallised from boiling nitrobenzene in red micro-crystals, m. p. 310° (decomp.) (Found: N, 16·7. $C_{16}H_{10}O_5N_4$ requires N, 16·5%).

The authors are indebted to the Charles Brotherton Trust for a Research Scholarship (to E. R. W.), to Imperial Chemical Industries Ltd., Dyestuffs Division, for gifts of chemicals, and to Mr. Frank Hobson for micro-analyses.

TECHNICAL COLLEGE, HUDDERSFIELD. [*Received, October 16th*, 1946.]

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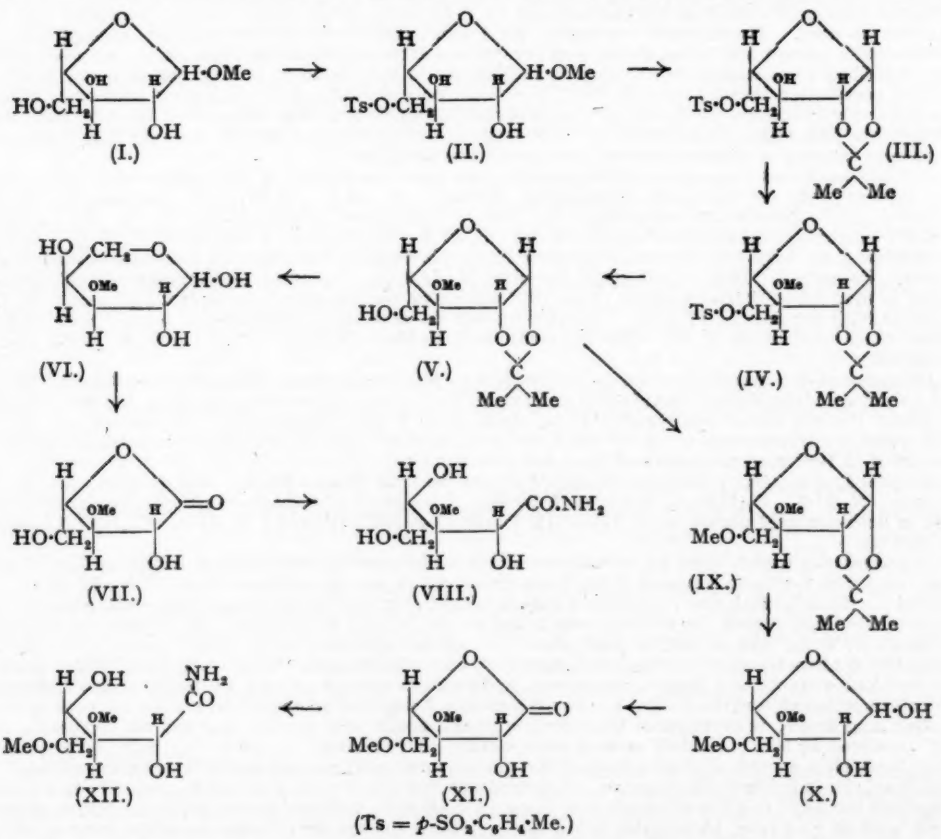
200. *The Synthesis of 3-Methyl and 3 : 5-Dimethyl l-Arabinose.*

By E. L. HIRST, J. K. N. JONES, and (MISS) E. WILLIAMS.

3-Methyl l-arabinose has been prepared from *5-p*-toluenesulphonyl 1 : 2-monoacetone *l*-arabinose. It forms a crystalline anilide and on oxidation gives *3-methyl l-arabonolactone*, further characterised as its crystalline *amide*. Methylation of *3-methyl* 1 : 2-*monoacetone l-arabinose* gives 3 : 5-*dimethyl* 1 : 2-*monoacetone l-arabinose* which on hydrolysis yields the known 3 : 5-dimethyl *l*-arabinose (White, *J. Amer. Chem. Soc.*, 1946, **68**, 272) which on oxidation gives 3 : 5-dimethyl *l*-arabonolactone, characterised as the crystalline amide and *phenylhydrazide*.

THE araban associated with pectin is known to be of the branched chain type (Hirst and Jones, *J.*, 1939, 454) since the methylated derivative gave on hydrolysis three products, namely, 2 : 3 : 5-trimethyl *l*-arabofuranose, 2 : 3-dimethyl *l*-arabinose, and a monomethyl derivative



the identity of which was not conclusively established though on the balance of evidence the methyl group was assigned tentatively to the 3-position. This monomethyl arabinose gave on

oxidation a furano-lactone, and since the free sugar had the properties of a derivative of arabopyranose it must be either 2- or 3-methyl *l*-arabinose. The latter possibility was thought to be the correct one since the non-crystalline amide prepared from the crude lactone gave a positive Weerman reaction indicating the presence of an α-hydroxy-amide. The synthesis of 3-methyl *l*-arabinose was accordingly undertaken in order to provide material of known constitution for comparison with that obtained from araban. The starting material in this synthesis was methyl *l*-arabofuranoside (I) (Baker and Haworth, *J.*, 1925, 365) which was converted into the syrupy 5-*p*-toluenesulphonyl derivative (II) by reaction with the calculated quantity of *p*-toluenesulphonyl chloride in dry pyridine. The known 5-*p*-toluenesulphonyl 1 : 2-monoacetone *l*-arabinose (III) [prepared previously from *l*-arabinose diethylmercaptal (Compton and Levene, *J. Biol. Chem.*, **1936**, **116**, 189)] was then prepared from (II) by reaction with acetone containing hydrogen chloride. Methylation of (III) with silver oxide and methyl iodide gave 5-p-*toluenesulphonyl* 3-*methyl* 1 : 2-*monoacetone* l-*arabinose* (IV) which on reductive alkaline hydrolysis (Compton and Levene, *loc. cit.*) gave 3-*methyl* 1 : 2-*monoacetone* l-*arabinose* (V). On acidic hydrolysis this product was converted into syrupy 3-*methyl* l-*arabinose* (VI). This compound formed a crystalline *anilide* on heating with alcoholic aniline and a crystalline *furanolactone* (VII) on oxidation with bromine water. A crystalline *amide* (VIII) was produced on reaction of the lactone with liquid ammonia (cf. Jellinek and Upson, *J. Amer. Chem. Soc.*, 1938, **60**, 356). This amide depressed the melting point of 2-methyl *l*-arabonamide and gave a positive Weerman test indicating the presence of a hydroxyl group on C2.

The monomethyl sugar isolated from the hydrolysis of peanut araban differs from 3-methyl *l*-arabinose and must therefore be 2-methyl *l*-arabinose. This has been subsequently confirmed by the synthesis of 2-methyl *l*-arabinose which was found to be identical with the monomethyl sugar isolated from methylated peanut araban (forthcoming publications).

3-Methyl 1 : 2-monoacetone *l*-arabinose (V) on further methylation gave 3 : 5-*dimethyl* 1 : 2-*monoacetone* l-*arabinose* (IX) which on hydrolysis gave 3 : 5-dimethyl *l*-arabinose (X); this on oxidation gave the corresponding furano-lactone (XI) which was smoothly converted into the α-hydroxy-amide (positive Weerman test) (XII) with liquid ammonia (cf. White, *loc. cit.*) and into the *phenylhydrazide* on heating with alcoholic phenylhydrazine.

Experimental.

5-p-*Toluenesulphonyl Methyl*-l-*arabofuranoside and* 5-p-*Toluenesulphonyl* 1 : 2-*Monoacetone* l-*Arabinose*.—Methyl-*l*-arabofuranoside (31 g.) was dissolved in dry pyridine (250 c.c.) and *p*-toluenesulphonyl chloride (37 g.), dissolved in pyridine (50 c.c.), was added at 20°. Heat was evolved, and the solution was then left overnight (20 hours). Next morning pyridine was removed under reduced pressure at 60°, and the syrupy residue dissolved in chloroform and the solution washed successively with N-sulphuric acid, saturated sodium hydrogen carbonate solution, and water. The chloroform extract [dried (Na_2SO_4) and filtered] was then concentrated under reduced pressure to the syrupy 5-*p*-toluenesulphonyl methyl-*l*-arabofuranoside (36 g.). The syrup (30 g.), without further purification, was dissolved in acetone (300 c.c.) containing dry hydrogen chloride (3 g.). After 70 hours the acetone solution was poured into excess of sodium hydrogen carbonate solution and the arabinose derivative extracted with chloroform. Concentration of the chloroform extracts [dried (Na_2SO_4)] gave 5-*p*-toluenesulphonyl 1 : 2-monoacetone *l*-arabofuranose, m. p. 130°, after recrystallisation from acetone–ether (yield, 21 g.) (cf. Compton and Levene, *loc. cit.*).

5-p-*Toluenesulphonyl* 3-*Methyl* 1 : 2-*Monoacetone* l-*Arabofuranose*.—5-*p*-Toluenesulphonyl 1 : 2-monoacetone *l*-arabofuranose (5 g.) was methylated by dissolution in methyl iodide (10 c.c.) and portionwise addition of silver oxide. The *product*, isolated in the usual manner, was recrystallised from acetone–light petroleum (b. p. 40—60°). The yield was quantitative, m. p. 101° (Found: C, 53·6; H, 6·1; OMe, 8·4; $C_{16}H_{22}O_7S$ requires C, 53·6; H, 6·2; OMe, 8·7%).

3-*Methyl* 1 : 2-*Monoacetone* l-*Arabofuranose*.—5-*p*-Toluenesulphonyl 1 : 2-monoacetone 3-methyl-*l*-arabofuranose (4 g.) was dissolved in methyl alcohol (50 c.c.) and water (20 c.c.), and sodium amalgam (40 g., 4%) added with stirring at 30° (cf. Compton and Levene, *loc. cit.*). The resultant monoacetone derivative was extracted with chloroform and the extracts were dried ($MgSO_4$) and filtered. Removal of the solvent left crude 3-*methyl* 1 : 2-*monoacetone* l-*arabinose* (1·8 g.), $n_D^{23°}$ 1·4565, which was purified by vacuum distillation; b. p. 120° (bath temp.)/2 mm., $n_D^{23°}$ 1·4572 (Found: C, 52·8; H, 7·5; OMe, 15·5. $C_9H_{16}O_5$ requires C, 52·9; H, 7·8; OMe, 15·2%).

3-*Methyl* l-*Arabinose*.—3-Methyl 1 : 2-monoacetone *l*-arabofuranose (0·73 g.) was dissolved in 20% acetic acid (20 c.c.) and boiled for 3 hours; $[\alpha]_D^{20}$ − 29° (initial value); + 95° (final value). The 3-*methyl arabinose* was isolated as a syrup on concentration of the solution in a vacuum; $[\alpha]_D^{20°}$ + 110° (*c*, 3·6 in water) (Found: OMe, 19·2. $C_6H_{12}O_5$ requires OMe, 18·9%). On being heated with alcoholic aniline (180 mg.) the sugar (111 mg.) gave a crystalline *anilide* (100 mg.), m. p. 117° after recrystallisation from alcohol (Found: C, 60·1; H, 7·3; N, 5·9; OMe, 12·6. $C_{12}H_{17}O_4N$ requires C, 60·2; H, 7·1; N, 5·9; OMe, 13·0%).

No crystalline phenylhydrazone could be isolated. On oxidation of the sugar with bromine water under the usual conditions 3-*methyl* l-*arabofuranolactone* was isolated as a crystalline solid (m. p. 71°) which was purified by sublimation in a vacuum, and then had m. p. 78° (constant value); $[\alpha]_D^{20°}$ − 74° (*c*, 0·34 in water), no observable change in 24 hours (Found: C, 44·3; H, 6·7; OMe, 19·2; equiv., 162.

$C_6H_{10}O_5$ requires C, 44·4; H, 6·2; OMe, 19·1%; equiv., 162). With liquid ammonia the lactone gave *3-methyl l-arabonamide*, m. p. 132°, after recrystallisation from alcohol–acetone (Found: C, 40·3; H, 7·3; N, 7·5; OMe, 17·1. $C_6H_{13}O_5N$ requires C, 40·2; H, 7·27; N, 7·8; OMe, 17·3%). This amide gave a positive Weerman test and depressed the m. p. of 2-methyl *l*-arabonamide.

3 : 5-*Dimethyl Monoacetone l-Arabofuranose*.—3-Methyl monoacetone *l*-arabinose (0·8 g.) was methylated with Purdie's reagents and the *product* (0·8 g.), isolated in the usual manner, was distilled under reduced pressure; b. p. 120° (bath temp.)/0·5 mm., $n_D^{22°}$ 1·4420 (Found: OMe, 28·1. $C_{10}H_{18}O_5$ requires OMe, 28·4%).

The above derivative (242 mg.) was boiled with 25% acetic acid (20 c.c.) for 3 hours; $[\alpha]_D^{20°}$ − 39°, unchanged on heating. The solution was concentrated under reduced pressure and the resultant 3 : 5-dimethyl *l*-arabofuranose purified by solution in acetone followed by filtration. The sugar had $n_D^{22°}$ 1·4600 (Found: OMe, 34·6. Calc. for $C_7H_{14}O_5$: OMe, 34·8%).

The sugar (200 mg.) was oxidised with bromine (1 c.c.) in water (5 c.c.) at 20° for 24 hours. Excess of bromine was removed by aeration and the last traces of bromine by passage of sulphur dioxide. The lactone was then removed from the aqueous solution by continuous extraction with chloroform. Concentration of the extracts gave crystalline 3 : 5-dimethyl *l*-arabonolactone, m. p. 73° (after sublimation in a vacuum), depressed to 50° on admixture with 2 : 5-dimethyl *l*-arabonolactone; $[\alpha]_D^{20°}$ − 83° (*c*, 0·12 in water), no observable change in 24 hours (Found: OMe, 33·9; equiv., 169. Calc. for $C_7H_{12}O_5$: OMe, 35·2%; equiv., 176). With liquid ammonia the lactone gave the corresponding amide, m. p. 144° (depressed to 120° on admixture with 2 : 5-dimethyl *l*-arabonamide), which gave a positive Weerman reaction (Found: C, 43·8; H, 7·6; N, 7·0; OMe, 31·2. Calc. for $C_7H_{15}O_5N$: C, 43·5; H, 7·8; N, 7·25; OMe, 32·1%).

The *phenylhydrazide*, m. p. 144° [depressed to 132° on admixture with the phenylhydrazide (m. p. 163°) of 2 : 5-dimethyl *l*-arabonic acid], was prepared by heating the lactone with an alcoholic solution of phenylhydrazine. It was recrystallised from acetone–ether (Found: C, 54·5; H, 6·8; N, 9·8; OMe, 21·6. $C_{13}H_{20}O_5N_2$ requires C, 54·8; H, 7·0; N, 9·9; OMe, 21·8%).

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THE UNIVERSITY, MANCHESTER. [*Received, October 29th*, 1946.]

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201. *The Constitution of Egg-plum Gum. Part I.*

By E. L. HIRST and J. K. N. JONES.

The gum exuded on the bark of the egg-plum has been examined and shown to consist of *l*-arabinose (3 parts), *d*-xylose (1 part), *d*-galactose (3 parts), and *d*-glucuronic acid (1 part). The aldobionic acid which is present in the portion of the gum molecule more resistant to acidic hydrolysis is *d*-glucuronosido-6-*d*-galactose identical with the aldobionic acid component present in gum arabic. The oxidation of the gum with potassium periodate has been studied.

IN common with many other fruit trees of the family *Rosaceæ* the egg or yellow Pershore plum tree forms a gum during the months of August and September. The gums from several other trees have already been examined (see Hirst and Jones, *J.*, 1946, 506) and it was of interest to determine whether Pershore plum gum has a similar constitution. The gums obtained from exudation usually contain small amounts only of nitrogenous materials, which may be part of the enzyme system originally responsible for their synthesis (M. Stacey, private communication). They are salts of acidic polysaccharides, the acidity being due to the presence of *d*-glucuronic or *d*-galacturonic acids or of their methyl ethers. *d*-Galactose and *l*-arabinose appear to be invariable constituents, whilst *d*-mannose, *d*-xylose, and *l*-rhamnose have also been detected in some plant gums.

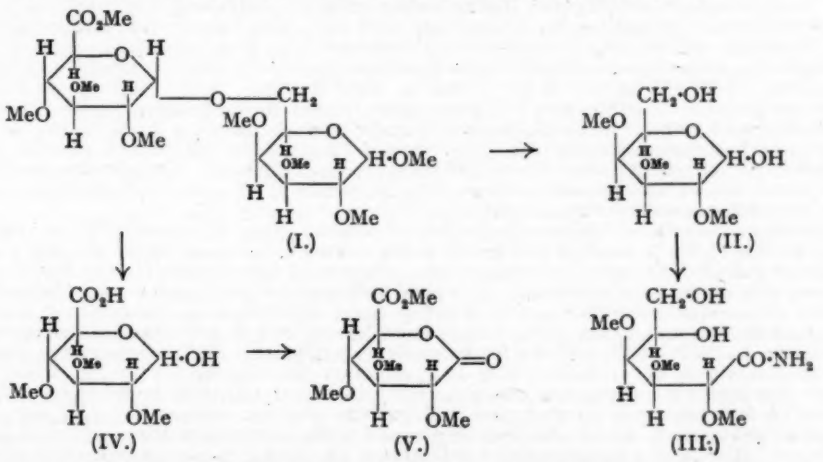
Purified ash-free Pershore plum gum is a white powder soluble in water giving an acidic solution which does not reduce Fehling's solution. So far as present evidence is available the gum so prepared appears to be a homogeneous substance, and attempts to extract from it by solvents fractions differing in elementary and physical properties have been unsuccessful. Gums obtained from several trees in the same area (Worcestershire) all have the same physical properties. The possibility remains, however, that the type of gum exuded by the tree may be dependent upon the type of stock on which the tree is grafted rather than upon the type of plum produced. Further work will be necessary before this can be settled.

The analytical figures for uronic acid residues (14·7%) and furfuraldehyde (25·5%) were obtained by boiling the polysaccharide with 12% hydrochloric acid and determining the amounts of carbon dioxide and furfuraldehyde formed. From these results estimates can be made of the pentose and the uronic acid content of the gum. An aqueous acidic solution of the ash-free polysaccharide undergoes graded hydrolysis on heating at 100°, the sugars obtained after hydrolysis consisting of a mixture of *l*-arabinose and *d*-xylose in the approximate proportion of 3 to 1. The remainder of the polysaccharide consists of *d*-galactose and *d*-glucuronic acid, since on

hydrolysis with N-sulphuric acid crystalline *d*-galactose is obtained together with an aldobionic acid having the structure *d*-glucuronosido-*d*-galactose (1 : 6 linkage) identical with the aldobionic acid in gum arabic. This structure, therefore, is an important feature in the mode of construction of the sugar residues in the repeating unit of the gum. It follows that Pershore plum gum resembles gum arabic, rather than damson or cherry gum (cf. Smith, *J.*, 1940, 1035), and in common with many other gums so far examined it contains a repeating unit consisting of two molecules of galactose united to an aldobionic acid. It is to be remembered, however, that owing to the difficulty encountered in isolating the aldobionic acid component of the gum in quantitative yield the possibility remains that some aldobionic acid other than 1 : 6-*d*-glucuronosido-*d*-galactose may be a component of the gum molecule. Conclusive proof is furnished below, however, of the presence of 1 : 6-*d*-glucuronosido-*d*-galactose as a part of the gum molecule.

The proof of the structure of the aldobionic acid follows from the observation that on methylation followed by hydrolysis of the methylated product (I), two products are obtained, namely, 2 : 3 : 4-trimethyl *d*-galactose (II), identified as its crystalline anilide and as the crystalline amide of 2 : 3 : 4-trimethyl *d*-galactonic acid (III), and 2 : 3 : 4-trimethyl *d*-glucuronic acid (IV), identified as the methyl ester of 2 : 3 : 4-trimethyl *d*-saccharolactone (V).

A quantitative estimation of the various sugars produced on hydrolysis of the original Pershore plum gum indicates that they were combined in the following proportions: *d*-glucuronic acid (1 part); *d*-galactose (3 parts); *l*-arabinose (3 parts); *d*-xylose (1 part).



When the gum is oxidised with potassium periodate under mild conditions, designed to prevent over-oxidation (see Brown, Dunstan, Halsall, Hirst, and Jones, *Nature*, 1945, **156**, 785) approximately one mol. of formic acid is produced and five mols. of periodate are consumed per equivalent of approximately 1220. The resulting oxidised polysaccharide, on being boiled under standard conditions with 12% hydrochloric acid, gives furfuraldehyde (10·8%) in a much diminished yield. This proves that some of those sugar residues in the original unoxidised polysaccharide which yield furfuraldehyde on distillation with hydrochloric acid have been destroyed during the oxidation. Since under the conditions of oxidation there is no continual rise in formic acid titre followed by a subsequent liberation of iodine, the glucuronic acid residue is not an end group (see Brown, Dunstan, Halsall, Hirst, and Jones, *loc. cit.*).

The oxidised polysaccharide on hydrolysis gives some *l*-arabinose (estimated as its benzoylhydrazone), but xylose could not be detected (see Breddy and Jones, *J.*, 1945, 738). The yields of *d*-galactose and *l*-arabinose indicated that at least 1·5 mols. of *d*-galactose and 0·5 mol. of *l*-arabinose per equivalent of 1220 are not oxidised by the periodate and therefore cannot possess adjacent hydroxyl groups in their combination in the gum molecule.

An examination of the product isolated from the reaction between the gum and triphenylmethyl chloride in pyridine shows that there are approximately four primary alcohol groups (Method of Linstedt, *Arkiv Kemi, Min. Geol.*, 1945, **20** *A*, No. 13) per equivalent of 1220.

Experimental.

Purification of Egg-plum Gum.—The gum, which resembled damson and cherry gums in properties, was purified by precipitation with alcohol from aqueous solutions to which hydrochloric acid had been

added (for further details see Hirst and Jones, *J.*, 1938, 1177). The gum gave no precipitate with calcium or copper salts but gave a white precipitate on addition of a large excess of thallium hydroxide. It was unaffected by takadiastase and pectinase at pH 7 at 35°. Two samples were prepared: (*A*) from gum collected from several different trees in two orchards, (*B*) from gum collected off one tree (see Table).

	Gum *A*.	Gum *B*.
$[\alpha]_D^{20°}$ (*c*, 2·4 as the sodium salt in water)	−27°	−25°
Equiv. (by titration with 0·1N-sodium hydroxide)	1228	1215
Furfuraldehyde	26%	25%
Uronic anhydride	—	14·7%
Galactan (from mucic acid determinations)	43%	44%

The samples from different trees are therefore substantially the same. The purified gum had a small iodine number (1·0 g. required 2·5 c.c. of 0·1N-iodine). [Found (crude gum): OMe, trace; N, nil.] The purified gum had a small methoxyl content (2·0%), probably owing to esterification during the purification process. Furfuraldehyde and uronic anhydride were determined after treatment of the purified polysaccharide with boiling 12% hydrochloric acid (Found: furfuraldehyde, 25·5; uronic anhydride or 2-ketohexonic acid, 14·7%). Methylpentose appears to be absent. [A substance yielding 14·7% of uronic anhydride or 2-ketohexonic acid and containing no other acidic residues should have an equivalent of 1197. Found by titration of the gum with alkali: equiv., 1222 (mean of two values).] This proportion of uronic anhydride accounts for 3·7% of the total furfuraldehyde, leaving 21·8% of furfuraldehyde contributed by the pentosan part of the polysaccharide, and since the greater part of the pentose present is *l*-arabinose (see below), the calculated anhydroarabinose content of the gum is approximately 44% (Calc. for a polysaccharide containing four pentosan units per repeating unit of equivalent 1190, 44·3%). Anhydrogalactose (estimated after oxidation to mucic acid), 43%.

Graded Hydrolysis of Egg-plum Gum.—(a) Egg-plum gum (50 g.) was heated with water (1½ l.) at 90—95°, the acidity of the solution being sufficient to bring about slow graded hydrolysis; the reaction was followed by polarimetric and iodometric observations: $[\alpha]_D^{20°}$ −27° (initial value); −24° (40 mins.); −9° (3·1 hrs.); +32° (15·5 hrs.); +41° (22 hrs.); +47° (34 hrs.); +50° (50 hrs.). A much slower hydrolysis continued beyond this stage. The increase in iodine titre was followed by titration of portions of the solution with 0·1N-iodine by Baker and Hulton's method (*Biochem. J.*, 1920, **14**, 754). Initial value (in c.c. 0·1N-iodine, calculated for 1 g. of gum) 2·5 c.c.; 6 c.c. (40 mins.); 15·5 c.c. (3·1 hrs.); 54 c.c. (15·5 hrs.); 58 c.c. (22 hrs.); 66 c.c. (34 hrs.); 72·6 c.c. (50 hrs.). The solution was evaporated at 40°/12 mm. to 500 c.c. and poured into alcohol (1½ l.); it then gave an alcohol-insoluble polysaccharide (*A*) (22·5 g.) which was washed with alcohol.

(b) *Reducing sugars obtained by graded hydrolysis.* The filtrate from (*A*) on concentration at 40°/12 mm. gave an acidic syrup which was dissolved in water, neutralised with barium carbonate, and filtered, and the filtrate poured into alcohol with stirring. The precipitated barium salt (*B*), which appeared to be the barium salt of the polysaccharide (*A*) which had escaped precipitation, was filtered off and the filtrate evaporated at 40°/12 mm. to a syrup which crystallised on standing. The crystalline solid (10·4 g.) was triturated with methyl alcohol and filtered off; it was identified as slightly impure *l*-arabinose, m. p. 154°; $[\alpha]_D^{20°}$ +96° (*c*, 3·8 in water; equilibrium value); diphenylhydrazone, m. p. 194°. The filtrate from the crystalline solid on evaporation gave a syrup (*C*) (15·2 g.) which had $[\alpha]_D^{20°}$ +38° and contained some oligosaccharide, since the iodine titre indicated the presence of only 9·3 g. of pentose. A furfuraldehyde determination indicated the presence of some 10·0 g. of pentose, whilst an arabinose estimation by means of diphenylhydrazine indicated the presence of approximately 5·0 g. of *l*-arabinose. Mucic acid was isolated after oxidation of a portion of the syrup with nitric acid, proving the presence of some 2·4 g. of galactose (free or combined). The syrup underwent further hydrolysis on heating with 0·5N-sulphuric acid for 1 hour. The optical rotation became constant at +60° and the iodine titre on a portion of the solution (*A*) showed that approximately 15 g. of reducing sugars were now present in solution. An estimation by means of diphenylhydrazine now showed the presence of 5·8 g. of *l*-arabinose, an increase of only 0·8 g. It can be inferred, therefore, that the oligosaccharide originally present contained *d*-galactose and *d*-xylose since the increase in reducing power of the solution is not due to increase of *l*-arabinose content but to an increase of *d*-galactose and *d*-xylose. A portion of the solution (*A*) after hydrolysis was neutralised with barium carbonate and filtered, and the filtrate evaporated to a syrup. *l*-Arabinose was removed from this syrup as its diphenylhydrazone, and the non-crystalline diphenylhydrazones remaining were then decomposed by warming with form aldehyde solution in the presence of acetic acid. The mixture was exhaustively extracted with ether and the aqueous solution evaporated to a syrup. [A portion of this gave the characteristic crystalline derivative of xylose, m. p. 210°, with a methyl alcoholic solution of benzaldehyde (see Breddy and Jones, *J.*, 1945, 738).] The syrup was boiled for 4 hours with 4% methyl alcoholic hydrogen chloride, and the solution was then neutralised with silver carbonate, filtered, and evaporated to a syrup which was methylated first by the thallium method (Menzies, *J.*, 1926, 937), and then with Purdie's reagents. The methylated sugars (4·0 g.) were distilled in a vacuum and gave a fraction (3·6 g.), b. p. 100° (bath temp.)/0·1 mm.; $n_D^{18°}$ 1·4438; $[\alpha]_D^{20°}$ +53° in water. This fraction was hydrolysed with N-hydrochloric acid (50 c.c.) on the boiling water-bath. $[\alpha]_D^{20°}$ fell from +53° to +44°. The free sugars were worked up in the usual manner and distilled in a vacuum; the distillate then crystallised. 2 : 3 : 4-Trimethyl *d*-xylose was recognised by its m. p. and mixed m. p. 91°, after recrystallisation from ether. The non-crystalline sugars gave some tetramethyl galactose anilide on heating with alcoholic aniline. This result, taken in conjunction with reducing values, furfuraldehyde yields, rotational values, and yield of *l*-arabinose diphenylhydrazone, indicates that the sugars produced on autohydrolysis consist of *l*-arabinose and *d*-xylose in the approximate proportion of three to one and that a small amount of galactose is also produced during the hydrolysis. A polysaccharide of equivalent weight 1222 and containing this amount of arabinose would yield 36·8% of arabinose on hydrolysis (Found: arabinose content, 32·4%).

(c) *Examination of the barium salt* (B). The barium salt (*B*) (10·4 g.) was obtained as a white powder

easily soluble in water, giving a yellow neutral solution, $[\alpha]_D^{20°}$ +4° (*c*, 3·3 in water). OMe, 3·0% (probably derived from adsorbed alcohol). It contained 11% of barium, gave 8·3% of furfuraldehyde on boiling with 12% hydrochloric acid, and on oxidation gave mucic acid equivalent to the presence of 50% of galactan. It was slightly reducing to Fehling's solution and reduced alkaline iodine (1 g. required 40·5 c.c. of 0·1N-iodine). On being heated with N-sulphuric acid for 3½ hours the barium salt underwent hydrolysis with an increase in iodine titre; initial value (in c.c. of 0·1N-iodine per 1 g. of barium salt) 41 c.c.; 58 c.c. (1½ hrs.); 65·4 c.c. (2 hrs.); 70·7 c.c. (3 hrs.); 74·4 c.c. (3½ hrs., constant value). The change in rotation was not observable owing to the colour of the solution. The solution was neutralised with barium carbonate, filtered, and evaporated to a syrup, which was extracted with methyl alcohol. Concentration of the extracts gave a syrup which soon crystallised. Trituration with alcohol gave crystalline *d*-galactose, $[\alpha]_D^{20°}$ +78° in water, m. p. and mixed m. p. 164°, in 42% yield calculated on the weight of the syrup isolated. (6·65 G. of barium salt gave 2·7 g. of syrup.) The non-crystalline barium-free residue showed $[\alpha]_D^{20°}$ +45° (*c*, 1·22 in water) and was 50% galactose (calc. on the yield of mucic acid obtained after oxidation with nitric acid under standard conditions). Mannose appeared to be absent since no mannose phenylhydrazone could be isolated after treatment of a portion of the non-crystalline syrup with phenylhydrazine solution. The remaining sugar was not identified but may have been *d*-xylose. The above figures show that hydrolysis of the barium salt with N-acid produced 29% of *d*-galactose calculated on the weight of the original barium salt.

The barium salt (3·40 g.) remaining after methyl alcoholic extraction was obtained as a white powder, very soluble in water, giving a yellow solution which reduced Fehling's solution vigorously on boiling. 1 G. of barium salt reduced 39 c.c. of 0·1N-iodine; this is equivalent to a molecular weight of 512. The solution showed $[\alpha]_D^{20°}$ +4° (*c*, 1·0 in water) (Found: OMe, 3·0%, but this value is probably not significant). The barium content of the salt was 15·7%, and on oxidation with nitric acid, mucic acid was produced, in amount showing the presence of some 40% of galactose residues (Calc. for the barium salt of an aldobionic acid; Ba, 16·2; galactose residues, 42%).

(d) *Polysaccharide* (A). This material (22·5 g.) was obtained as a white powder, easily soluble in water giving a brown solution with an acidic reaction to Congo-red. On boiling it with 12% hydrochloric acid, furfuraldehyde (8·1%) and carbon dioxide (equivalent to the presence of 26·0% of uronic anhydride) were evolved. $[\alpha]_D^{20°}$ +24° (in water, *c*, 0·7). The polysaccharide on being heated with nitric acid (*d* 1·2) gave mucic acid equivalent to the presence of some 50% of anhydrogalactose; this figure is low owing to the difficulty experienced in hydrolysing polysaccharide (*A*) completely. The equivalent (by titration with 0·1N-sodium hydroxide) was 640 (Calc. for a repeating unit containing three hexose residues and a uronic acid residue, 662). On titration with alkaline iodine by the method of Bergmann and Machemer, 1 g. of polysaccharide (*A*) required 23 c.c. of 0·1N-iodine.

Polysaccharide (*A*) (1·49 g.) underwent hydrolysis on heating at 90° with N-sulphuric acid (50 c.c.). $[\alpha]_D^{20°}$ changed from +28° (initial value) to +30° (3 hrs., constant value). The iodine titre (in c.c. of 0·1N-iodine per g. of polysaccharide) was 23 c.c. (initial value); 47 (½ hr.); 57 (1 hr.); 73 (2 hrs.); 75 (3 hrs.). The cooled solution was neutralised with barium carbonate, filtered, and evaporated to dryness, and the residue exhaustively extracted with alcohol. Concentration of the extracts gave crystalline *d*-galactose (0·4 g.), m. p. 164°, $[\alpha]_D^{20°}$ +80° (*c*, 1·3 in water). The residual barium salt showed $[\alpha]_D^{20°}$ ±0° (*c*, 2·0 in water). On oxidation with nitric acid (*d* 1·2) it gave mucic acid equivalent to the presence of some 50% of anhydrogalactose, and contained 16·3% of barium (Calc. for a barium aldobionate: Ba, 16·2%).

The barium salt of the aldobionic acid from polysaccharide (*A*) underwent further hydrolysis with much decomposition on being heated at 95° with 4N-sulphuric acid for 24 hours. From the solution, after neutralisation with barium carbonate and filtration, *d*-galactose was obtained in crystals, m. p. 163°, $[\alpha]_D^{20°}$ +77° (*c*, 1·1, in water), and as its phenylmethylhydrazone, m. p. 190°. The barium salt of the uronic acid was identified as barium glucuronate (see below). The total percentage yields of *d*-galactose and barium glucuronate isolated were small, but the proof of the presence of these two compounds combined as an aldobionic acid is furnished by a study of the hydrolysis products of the methylated aldobionic acid.

Methyl heptamethyl aldobionate. The barium salt of the aldobionic acid (3·3 g.) was dissolved in water and the barium precipitated as sulphate by the addition of the calculated quantity of 0·1N-sulphuric acid. The solution was filtered, and the filtrate evaporated to a syrup which was simultaneously esterified and converted into the glycoside by boiling with 2% methyl alcoholic hydrogen chloride for 20 hours. This time of esterification was too long, since much hydrolysis to monosaccharides had taken place. The solution was neutralised with silver carbonate, filtered, and evaporated to a syrup which was methylated by means of thallium hydroxide and methyl iodide in the usual manner (for details, see Hirst and Jones, *loc. cit.*). The methylated material was extracted with acetone, the solvent boiled off, and the residual syrup (2·85 g., $n_D^{17°}$ 1·4545) distilled in a vacuum giving:

Fraction I (2·0 g.). Mainly monosaccharides, b. p. 130° (bath temp.)/0·001 mm.; $n_D^{20°}$ 1·4495.

Fraction II (0·69 g.). Methyl heptamethyl aldobionate, b. p. 180° (bath temp.)/0·001 mm.; $n_D^{20°}$ 1·4680; $[\alpha]_D^{20°}$ +40° (*c*, 1·3 in water) (Found: OMe, 51·3; equiv., 470. Calc. for $C_{20}H_{36}O_{11}$: OMe, 53·0%; equiv. 468).

The methyl heptamethyl aldobionate (Fraction II) (0·67 g.) was hydrolysed by boiling it with 2N-hydrochloric acid (50 c.c.) for 10 hours. The rotation ($[\alpha]_D^{20°}$) rose from +40° to +46° in 3 hours, after which the solution became too dark for polarimetric observation. The cooled solution was neutralised with silver carbonate and filtered before and after the passage of hydrogen sulphide. The solution was then neutralised with barium carbonate and filtered, and the filtrate evaporated to a syrup which was exhaustively extracted with ether. The extracts on concentration gave a syrup {0·27 g.; $[\alpha]_D^{20°}$ +65° (*c*, 1·97 in water); OMe, 41%} which was mainly 2 : 3 : 4-trimethyl *d*-galactose, since after heating a portion of it with alcoholic aniline, the characteristic 2 : 3 : 4-trimethyl *d*-galactose anilide, m. p. and mixed m. p. 169°, was isolated. The rotation of the isolated sugar is low, probably because of contamination with a little 2 : 3 : 5-trimethyl *d*-galactose due to methyl furanoside formation on boiling the aldobionic acid with methyl alcoholic hydrogen chloride (cf. Challinor, Haworth, and Hirst, *loc. cit.*). The

sugar on oxidation with bromine water gave a lactone, $[\alpha]_D^{20°}$ +95° in water (initial value), which with liquid ammonia gave 2 : 3 : 4-trimethyl *d*-galactonamide, m. p. and mixed m. p. 165°.

The barium salt remaining after ether extraction was dissolved in water and barium removed as sulphate. The trimethyl *d*-glucuronic acid remaining in solution was oxidised with bromine water and the 2 : 3 : 4-trimethyl *d*-saccharic acid isolated in the usual manner and esterified with methyl alcoholic hydrogen chloride, and the dimethyl ester distilled in a vacuum; b. p. 120° (bath temp.)/0·01 mm. The distillate crystallised on standing. After separation on a tile, the methyl ester of 2 : 3 : 4-trimethyl *d*-saccharolactone was obtained, m. p. 110° not depressed on admixture with an authentic sample. This aldobionic acid was therefore *d*-glucuronosido-1 : 6-*d*-galactose.

Oxidation of the Gum with Potassium Periodate.—(*a*) The neutral gum (0·25 g.) was dissolved in water (250 c.c.) containing potassium chloride (1 g.) and sodium periodate (20 c.c.; 0·3M) and shaken for 10 days at 15°. Portions (10 c.c.) were taken out at intervals, ethylene glycol was added to destroy excess of periodate, and the formic acid was titrated with 0·01N-barium hydroxide [Titre: 0·65 c.c. (24 hrs.); 0·85 c.c. (72 hrs.); 0·9 c.c. (96 hrs.); 0·9 c.c. (192 hrs. constant)].

(*b*) The gum (1·399 g.) was dissolved in water (250 c.c.) containing potassium chloride (5 g.) and shaken for 8 days at 17° with sodium periodate (50 c.c.; 0·236M). At the end of this time titration showed that periodate equivalent to 125·6 c.c. of 0·1N-arsenite had been used in oxidising the gum.

In a similar experiment the gum (0·504 g.) required for oxidation periodate equivalent to 47·0 c.c. of 0·1N-arsenite. If, as indicated above, the gum contains four mols. of pentose, three mols. of hexose and one mol. of uronic acid per repeating unit of equivalent 1190, these figures show that an average of 1·07 mol. of formic acid is produced and an average of 5·2 mols. of periodate are consumed per repeating unit.

(*c*) The gum (0·5 g.) was oxidised in the usual manner for 200 hours. The solution was then cooled to 0° and filtered from potassium periodate. Slight excess of a solution of barium chloride was then added, and the precipitated barium iodate and periodate filtered off. The last traces of periodate and iodate were destroyed by bubbling sulphur dioxide through the filtrate which was then concentrated in a vacuum to a dry solid. A furfuraldehyde determination was then carried out in the usual manner.

In a second experiment the gum (0·5 g.) was oxidised as described above and the salts were then removed by dialysis [Found: Furfuraldehyde, 10·0 and 11·6. Calc. (for the loss of two pentose units and one uronic acid unit by periodate oxidation), 10·9; (for the loss of two pentose units only), 14·6%].

Hydrolysis of the oxidised gum. The oxidised gum (2·864 g.; see above for preparation) was hydrolysed by boiling with N-sulphuric acid (50 c.c.) for 48 hours. Since the solution became very dark and since the polysaccharide did not completely dissolve it was not possible to tell when the hydrolysis was completed. Sulphuric acid was precipitated by the addition of barium hydroxide, and the solution, after filtration, was concentrated in a partial vacuum to a solid. This residue was extracted exhaustively with methanol, and the extracts were concentrated under diminished pressure, to a syrup which was made up to 10 c.c. with water.

A galactose estimation on the solution (4 c.c.) gave 387 mg. of phenylmethylhydrazone, m. p. 186°. This is equivalent to approximately 1·5 mols. of galactose (per repeating unit of equiv. 1220) in the oxidised gum.

An arabinose estimation on the solution (2 c.c.) gave *l*-arabinose benzoylhydrazone (20 mg.), m. p. 180° (decomp.), equivalent to 33 mg. of *l*-arabinose, corresponding to 0·5 mol. of *l*-arabinose residues (per repeating unit of equiv. 1200) in the oxidised gum. This value is certainly low owing to the conversion of, arabinose into furfuraldehyde during the hydrolysis, and the true figure is probably nearer one mol.

No xylose could be detected (as the dibenzylidene dimethyl acetal, Breddy and Jones, *J.*, 1945, 738).

Estimation of $-CH_2{\cdot}OH$ *Groups in the Gum.* (Method of Lindstedt, *Arkiv Kemi, Min. Geol.*, 1945, **20** *A*, No. 13.)—The gum (1·65 g.) was suspended in pyridine (30 c.c.) and triphenylmethyl chloride (5 g.) added, and the mixture heated on a water-bath at 100° for 12 hours. The mixture was then poured into cold water (200 c.c.) and the product filtered off and washed with alcohol and ether. The last traces of triphenylmethylcarbinol were removed by exhaustive extraction with alcohol and the product dried in a vacuum (yield 2·46 g.).

This product was shaken with concentrated sulphuric acid (10 c.c.) for 12 hours. The resultant thick black solution was poured into water and the crude triphenylmethylcarbinol filtered off, washed with water and dilute ammonia, and weighed. The weight of pure triphenylmethylcarbinol was then obtained by exhaustive extraction from the filtered solid with alcohol (Found: 1·05 g. A polysaccharide containing four primary alcohol groups per repeating unit of 1220 requires 1·04 g.).

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202. *The Hydrogenation of Furfuraldehyde to Furfuryl Alcohol and Sylvan (2-Methylfuran).*

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Both sylvan and furfuryl alcohol are formed in the hydrogenation of furfuraldehyde in the vapour phase at atmospheric pressure with a copper catalyst. The alcohol is formed in the lower temperature range (<200°) and sylvan at intermediate temperatures (~250°). At higher temperatures (>300°) furfuryl alcohol tends once more to be the main product, but operation under these conditions leads to a rapid decline in catalyst activity. A regular change from the predominance of sylvan to that of furfuryl alcohol occurs with an increase in the amount of

alkali added to the catalyst. The presence of chromium oxides, on the other hand, favours the formation of sylvan. A theory of hydrogenation is proposed to account for these effects.

THE hydrogenation of furfuraldehyde in the vapour phase at atmospheric pressure is reported to give sylvan (2-methylfuran) in excellent yield (Burnette, *Iowa State Coll. J. Sci.*, 1944, **19**, 9; Wilson, *J.*, 1945, 61) but other workers find that furfuryl alcohol may be the main product (Ricard and Guinot, F.P. 639,756; U.S.P. 1,739,919; D.R.-P. 528,820; Lazier, U.S.P. 2,077,422). Where this is so, an increased overall conversion of furfuraldehyde into sylvan may be obtained by the further passage of the alcohol over the catalyst or by working at a higher catalyst temperature :

$$C_4H_3O{\cdot}CHO + H_2 = C_4H_3O{\cdot}CH_2{\cdot}OH;\ \Delta H = -18{\cdot}5 \text{ kcals.} \quad (1)$$

$$C_4H_3O{\cdot}CHO + 2H_2 = C_4H_3O{\cdot}CH_3 + H_2O;\ \Delta H = -34 \text{ kcals.} \quad (2)$$

The present work aimed at a more detailed and systematic investigation of the catalytic hydrogenation of furfuraldehyde in the vapour phase. The emphasis was placed on those factors which determine the main product to be furfuryl alcohol or sylvan. The results obtained in this and related work are considered from the standpoint of a theory of catalysis involving the intermediate formation of radicals.

EXPERIMENTAL.

Furfuraldehyde.—The commercial material was distilled at 30—40 mm. The colourless distillate had $d_4^{20°}$ 1·160, $n_D^{20°}$ 1·525, b. p. 161—162°, and contained 0·003% of sulphur.

Hydrogen.—Electrolytic cylinder gas was used containing about 0·001% of carbon monoxide.

Catalysts.—Five different copper catalysts were used.

Copper–aluminium alloy catalysts were prepared from chill castings. The casting was crushed to give ¼—½″ diameter granules and then activated by treatment with 0·4% aqueous sodium hydroxide at 100° : this removes aluminium from the surface layers but leaves the granule size unchanged (cf. Bag and Egupov, *Uspekhi Khimii*, 1945, **14**, No. 1, 56). In these catalysts both the original alloy composition and the amount of aluminium extracted may be varied. The alloys examined contained 34, 55, and 62% of copper and the aluminium extracted varied from 5 to 35%. After activation, the granules were washed with water to remove alkali. The catalyst may be stored under water until required.

Three copper–alumina catalysts were prepared. (*A*) Cu–Al_2O_3 was prepared by dehydrating alumina trihydrate to the monohydrate, moulding it into ⅛″ × ⅛″ cylinders, and then dehydrating it to γ-Al_2O_3 by heating to 750°. The pellets were impregnated with copper nitrate to give 20% of Cu calculated on Al_2O_3. (*B*) Cu–Al_2O_3 was prepared by impregnating the commercial activated alumina supplied by the Aluminium Ore Company of America with copper nitrate to give a 20% copper content. (*C*) Cu–Al_2O_3 was a co-precipitated catalyst formed by addition of sodium carbonate to the mixed metal nitrates. The precipitate, after being washed, was heated to 350°, and then made into cylindrical pellets as above.

A copper chromite catalyst, magnesium promoted, was prepared in similar fashion to that described by Adkins, Connor, and Folkers (*J. Amer. Chem. Soc.*, 1932, **54**, 1138). The Cu : Cr : Mg atom ratio in this catalyst was 1 : 1·05 : 0·04. The catalyst was used in the form of $\frac{3}{16}$″ × $\frac{3}{16}$″ pellets.

The copper–alumina and copper–chromite catalysts were reduced by hydrogen before use. Care was taken in this operation not to exceed 400°, the maximum reduction temperature normally being 350°.

The pelleted catalysts may be modified by impregnation with soluble salts. This is readily accomplished by adding to the pellets a volume of aqueous solution such that complete absorption occurs.

Apparatus.—Experiments were carried out in a continuous manner by passage of furfuraldehyde vapour and hydrogen downwards through the catalyst mass. Two types of apparatus were used, in both of which the catalyst tube was vertical. In one, the catalyst, supported on silica granules, was contained in a " Pyrex " glass tube (42″ × 1¼″) (Fig. 1). The space above the catalyst was packed with silica granules, and acted as a vaporising and pre-heating zone. The temperature through the contact material was measured by a movable iron–constantan thermocouple held in a glass sheath disposed axially down the tube. The catalyst volume was normally 200 ml. The catalyst tube was surrounded by an iron tube heated by three electrical windings independently controlled. In the absence of a pronounced heat of reaction, this arrangement enables a uniform temperature to be maintained throughout the catalyst mass. This apparatus will subsequently be referred to as the " standard " one.

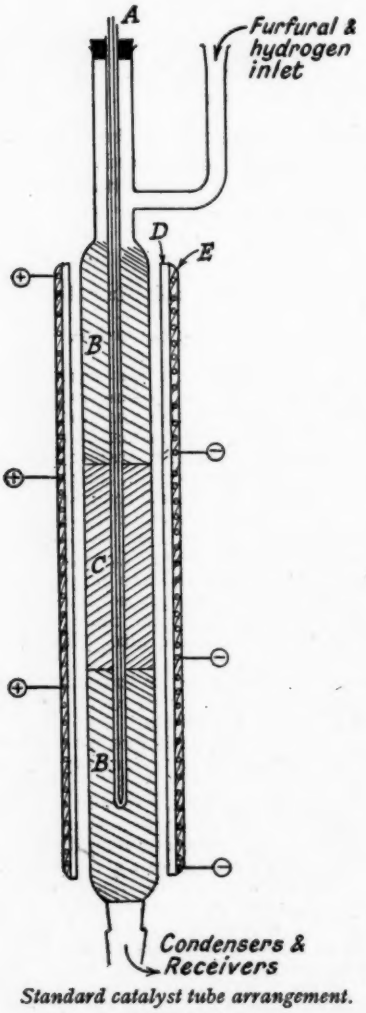
The other apparatus comprised a " Staybrite " metal catalyst tube (45″ × 1″) to which was welded a metal jacket (Fig. 2). The catalyst arrangement was as in the glass tube but with the thermocouple sheath of " Staybrite " metal. The jacket was filled with liquid of b. p. suitable to maintain the reaction temperature. The vapour arising from the boiling liquid was condensed and returned. The liquid was heated to the b. p. by electrical windings on the exterior of the jacket. In exothermic reactions the heat evolved is removed by vaporisation of the surrounding liquid. The exterior surface of the catalyst tube is, in this way, held at a constant temperature regardless of the thermal nature of the reaction. This apparatus will subsequently be referred to as the " jacketed " type.

For both catalyst tube arrangements, furfuraldehyde was fed from a calibrated vessel by displacement with hydrogen evolved electrolytically. Hydrogen was admitted to the tube through an integrating rotary gas-meter capable of measuring rates up to about 100 l./hr. The products from the catalyst tube passed through a water-cooled double-surface condenser to a glass receiver. Unreacted hydrogen was passed through two receivers immersed in ice and water and two receivers immersed in solid carbon dioxide–methanol. Material entrained by the gas was recovered in these receive s. The volume of

unreacted hydrogen was measured by an integrating rotary gas-meter. The volume of hydrogen absorbed during the hydrogenation gives an excellent indication of the course of the reaction.

Analysis of Products.—Gaseous products were analysed in an Orsat apparatus. The liquid products were homogeneous if the furfuraldehyde were largely unchanged or if furfuryl alcohol was the main product. With sylvan as the main product, a lower aqueous layer was obtained. Small amounts of aqueous top layer were observed when the product was a mixture of sylvan, furfuryl alcohol, and some

FIG. 1.

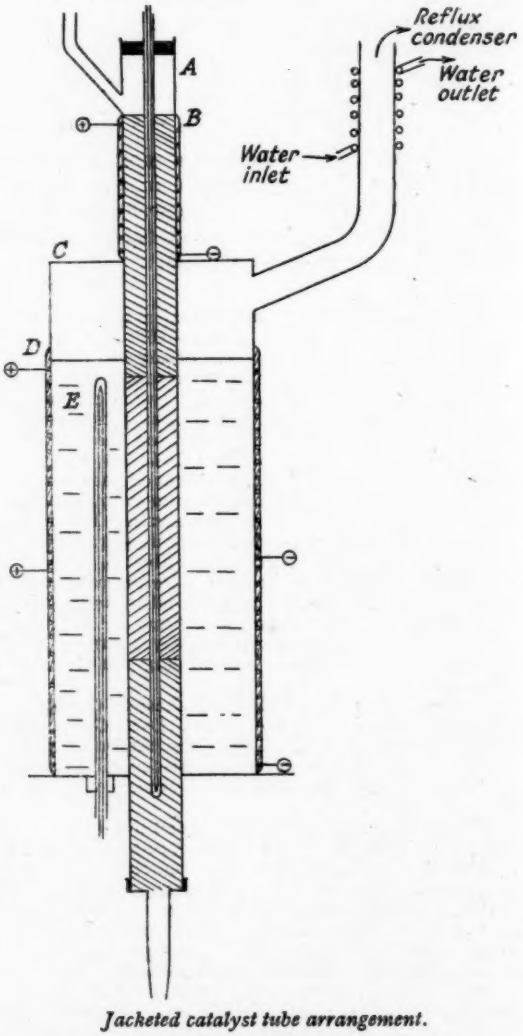


Standard catalyst tube arrangement.

Key to Fig. 1.

A = *Thermocouples.*
B = *Silica granules.*
C = *Catalyst.*
D = *Iron tube.*
E = *Electrical windings.*

FIG. 2.



Jacketed catalyst tube arrangement.

Key to Fig. 2.

A = *Metal catalyst tube.*
B = *Vapouriser.*
C = *Metal jacket.*
D = *Jacket heaters.*
E = *Temperature control liquid.*

unreacted aldehyde. In addition to sylvan and furfuryl alcohol, furan and pentanone-2 (Burnette, *loc. cit.*) were sometimes formed in small amount, and a pentanol in traces. Sylvan appears to be the precursor for pentanone-2.* Furfuraldehyde may suitably be estimated in a homogeneous product by titration of the acid liberated on reaction with hydroxylamine hydrochloride. This determination is carried out at room temperature, for, under reflux conditions, furfuryl alcohol also reacts with hydroxyl-

* Sylvan can be hydrogenated in good yield to pentanone-2 by using a copper catalyst (unpublished work).

amine hydrochloride liberating approximately 1 mol. of hydrochloric acid per mol. of alcohol. This effect is presumably due to a ring opening reaction (Pummerer, *Ber.*, 1923, **56**, 999). Although both furfuraldehyde (Hughes and Acree, *Ind. Eng. Chem. Anal.*, 1934, **6**, 123; *Cereal Chem.*, 1941, **18**, 572) and furfuryl alcohol may react with bromine, the use of pyridine sulphate bromide as reagent (Fitelson, *J. Assoc. Off. Agric. Chem.*, 1943, **26**, 499; Wilson and Nisbet, *Analyst*, 1946, **71**, 183) limits the attack almost completely to furfuryl alcohol. (A fuller description of these analytical methods will shortly be published.)

In addition to the chemical analysis of a homogeneous product, both it and the heterogeneous one were fractionated in a column equivalent to about 20 theoretical plates. When 100° was reached, the distillation was continued at about 20 mm. to separate unreacted furfuraldehyde from furfuryl alcohol (Dunlop and Trimble, *Ind. Eng. Chem.*, 1940, **32**, 1000). Distillative analysis is not straightforward, for furan, sylvan (Pranishnikov and Genin, *J. Appl. Chem. U.S.S.R.*, 1940, **13**, 140), pentanone-2, pentanol-2, and furfuraldehyde all form azeotropes with water. As the water content of these azeotropes exceeds the water miscibility at room temperature the distillates separate into two layers (see Table I).

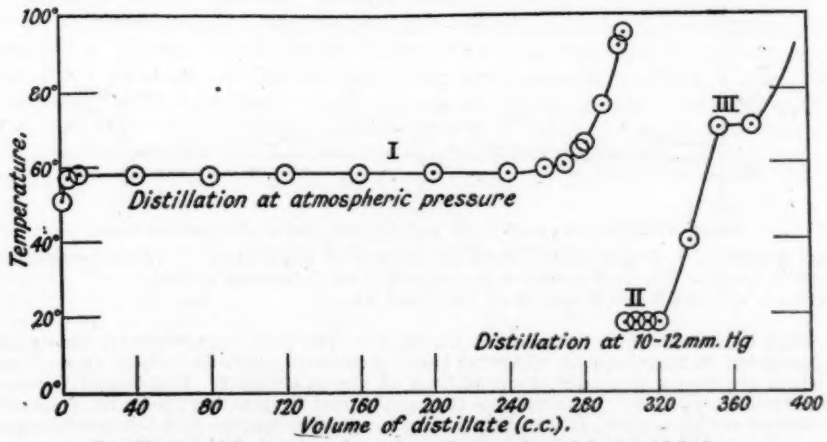
TABLE I.

Water azeotropes: boiling point and composition.

Compound.	B. p.	Water azeotrope. B. p.	Water content (wt. %).
Furan	32°	30·5°	1·2
Sylvan	63	58	4·9
Pentanone-2	102·3	82·9	13·5
Pentanol-2	119·3	92·5	38·5
Furfuraldehyde	162	98	64
Furfuryl alcohol	171	—	—

The low b. p.s of furan and sylvan make their complete recovery during distillation difficult unless cooled condensers and receivers are used. A loss of 5% of sylvan under normal distillation conditions

FIG. 3.



Distillation of the product from the hydrogenation of furfuraldehyde.

I, *Sylvan–water azeotrope*; II, *Furfuraldehyde–water azeotrope*; III, *Furfuryl alcohol.*

readily occurs. When distilled, furfuraldehyde and furfuryl alcohol tend to polymerise, particularly where impregnated catalysts are used which decompose to give acid vapours on heating. This effect was minimised by addition of sodium carbonate to the receiver in which the liquid products were collected. The results of a typical distillation are given in Fig. 3.

It is clear that where a mixture of products is obtained a rigorous analysis is difficult. When either sylvan or furfuryl alcohol alone is formed the interpretation is greatly simplified.

Results.—The terms pass conversion and yield are used to denote, respectively, the percentage of furfuraldehyde used in a single passage over the catalyst and the per cent. of the theoretical yield based on the amount of furfuraldehyde converted. As some 100—150 g. of furfuraldehyde were used in a normal experiment, yields were calculated on the weight and analysis of product obtained so as to counteract the large effect that small weight losses would otherwise have.

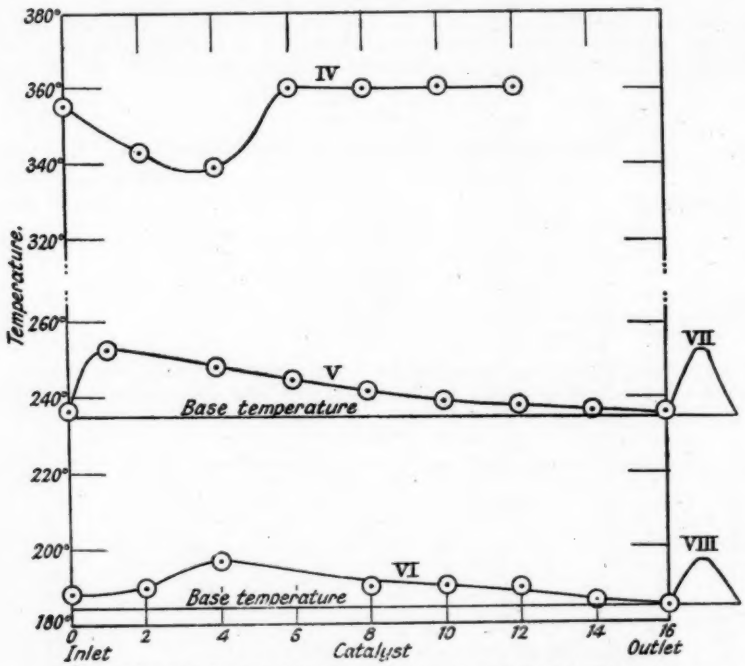
The small-scale experiments here described were, in part, the basis for the large-scale preparation of sylvan and furfuryl alcohol. The yields obtained equalled any now given.

Space velocity refers to the volume of furfuraldehyde fed per unit bulk volume of catalyst space per hour.

There is frequently some ambiguity in published work on catalytic reactions as to the interpretation to be placed on the temperature measurements. Normally, only one temperature is given, although it is

evident that the catalyst is not being worked under isothermal conditions. In this work the reaction temperature given is the maximum or peak temperature of the catalyst averaged from recorded half-hourly readings during experiments of a normal duration of 6 hours. In exothermic reactions the catalyst temperature rises rapidly at the beginning of the catalyst mass and then falls off slowly to a steady value which we term the " base " temperature. Typical temperature profiles measured longitudinally down the catalyst mass are given in Fig. 4. Curve VI shows the peak temperature to be only a few degrees above the base temperature for the hydrogenation to furfuryl alcohol ($\Delta H^{\circ}_{298} = -18{,}500$ cals.). The higher exothermicity accompanying sylvan formation ($\Delta H^{\circ}_{298} = -34{,}000$ cals.) is evident from curve V,

FIG. 4



Catalyst temperature profiles for endothermic and exothermic reactions.

Longitudinal profiles: IV, *Dehydrogenation and dehydration of* isopropanol: V, *Hydrogenation of furfuraldehyde to sylvan:* VI, *Hydrogenation of furfuraldehyde to furfuryl alcohol.*
Radial profiles: VII *and* VIII, *Reactions as for* V *and* VI.

Fig. 4, in which the temperature increment is about 20°. The peak temperature is the important one from the standpoint of reaction rate, while the base temperature controls the pass conversion in those reactions which are reversible under the conditions of the experiment. Reaction (1) is reversible in this sense, but not reaction (2). In addition to the longitudinal temperature profile there is a corresponding radial gradient at right angles. The radial gradient is a maximum at the peak temperature and becomes almost zero in the region of the base temperature. The maximum radial gradients are shown alongside curves VI and V in Fig. 4.

In an endothermic reaction the temperature falls at the beginning of the catalyst mass and rises slowly to the base temperature. This is shown in curve IV, Fig. 4.

DISCUSSION.

(1) *Equilibria in the Conversion of Furfuraldehyde into Furfuryl Alcohol and Sylvan.*—Only the scantiest of thermodynamic data are available for furfuraldehyde and furfuryl alcohol, and none has been published for sylvan. Early work by Landrieu, Baylocq, and Johnson (*Bull. Soc. chim.*, 1929, **45**, 36) gives the heat of combustion of liquid furfuraldehyde and furfuryl alcohol. Miller (*Iowa State Coll. J. Sci.*, 1936, **10**, 91) gives the free energy of formation of the liquids as -32 and $-45{\cdot}2$ kcals., respectively, at 298° K. The latent heat of furfuraldehyde alone has been published (Crawford, *Ind. Eng. Chem.*, 1940, **32**, 1280).

For the hydrogenation in the vapour phase of furfuraldehyde to furfuryl alcohol, we derive $\Delta H^{\circ}_{298} = -18{\cdot}5$ kcals. from the combustion data. In making this calculation we have taken the latent heat of the alcohol to be 1 kcal. greater than that of the aldehyde. From bond energies (Pauling, " The Nature of the Chemical Bond," 1939, Chaps. 2 & 4) we obtain $\Delta H^{\circ}_{291} =$

−17·6 kcals. Both these values are higher than those given for similar reactions (Cubberley and Mueller, *J. Amer. Chem. Soc.*, 1946, **68**, 1149). The resonance energy of sylvan being taken as 24·5 kcals. (Pauling, *J. Amer. Chem. Soc.*, 1939, **61**, 1778), the hydrogenation heat of furfuraldehyde vapour to sylvan is found to be $\Delta H^{\circ}_{291} = -34$ kcals.

The Nernst approximate theorem gives 98 and 60% pass conversion for reaction (1) at 0° and 300°, respectively, but the use of five times the theoretical amount of hydrogen raises the conversion to 96% at 250° at 1 atm.

The Nernst theorem applied to reaction (2) shows conversion to be substantially complete up to 300° at atmospheric pressure even with a stoicheiometric ratio of hydrogen.

(2) *The Effect of Catalyst Temperature on the Course of Hydrogenation.*—Experiments carried out with copper–aluminium alloy catalysts (Table II) show the activity of the activated alloy to vary little with composition in the range 34—62% of copper (S.118, S.240, and S.244). The activity is, however, dependent on the amount of aluminium removed during the activation procedure. While it is very small for the original alloy (S.198), the removal of only 5% of aluminium (S.155) gives an active catalyst. Somewhat greater activity is apparent at higher extractions (S.118 and S.162), where, however, the copper surface tends to be removable by abrasion. A convenient extraction is 10—20% and, particularly with the lower value, a catalyst which has become inactive in use may be further extracted to restore the activity. When the activity declines owing to a deposition of carbonaceous material, a high activity results from treatment with air at about 400° followed by reduction with hydrogen (S.126).

The results in Table II show sylvan to be the major product with the alloy catalyst operated in the region of 250° regardless of either the alloy composition or the amount of aluminium extracted. The treatment with air of a catalyst whose activity has declined in use, due to the deposition of carbonaceous material (S.124), leaves unaffected the formation of sylvan in high yield, as does the exposure of the catalyst to air before reaction (S.123). Although these changes in catalyst composition and treatment failed to affect the formation of sylvan, yet experiments conducted at temperatures below about 250° effected a marked change in the products of hydrogenation. At about 200° (S.270) furfuryl alcohol becomes the major product. Whilst this behaviour is not unexpected from previous work, it was surprising to find that at 300° (S.124) the activity of the catalyst declined steadily during operation. Further, this decline in activity was accompanied by an increase in the yield of furfuryl alcohol and a decrease in that of sylvan. The activity of the catalyst could be completely restored by careful treatment with air at a

TABLE II.

Examination of Cu–Al *alloy catalysts.**

Expt. No.	Initial alloy composn. Cu, %.	Al removed, %.	Liquid space velocity (hrs.$^{-1}$).	Temp.	Molar ratio, H_2/aldehyde.	Duration of expt. (hrs.).	Pass conv. (%).	Yield (%). Sylvan.	Yield (%). Furfuryl alcohol.	Remarks.
S.198	55	Nil	0·22	264°	7·1	1·0	~10	—	—	Al extraction variable.
S.155	55	5	0·16	253	7·3	6·0	90·5	89	2	
S.118	55	20	0·19	248	6·1	6·0	97·6	88	5	
S.162	55	35	0·12	243	6·8	6·25	99	88	3	Alloy composition variable.
S.240	34	20	0·17	254	7·1	5·0	91	89	3	
S.244	62	20	0·15	255	5·8	6·5	99·6	84	6	
S.124	55	20	0·27	300	5·4	6·25	27·6	42	46	Temp. variable.
S.270	55	20	0·18	193	5·7	4·0	63	29	66	
S.123	55	20	0·19	249	4·9	6·25	91·8	87	8	Catalyst exposed to air 30 hrs. before experiment.
S.126	55	20	0·17	250	5·3	6·5	98	87	5	Catalyst *ex* S.124; air-treated at 400°, reduced at 350°.

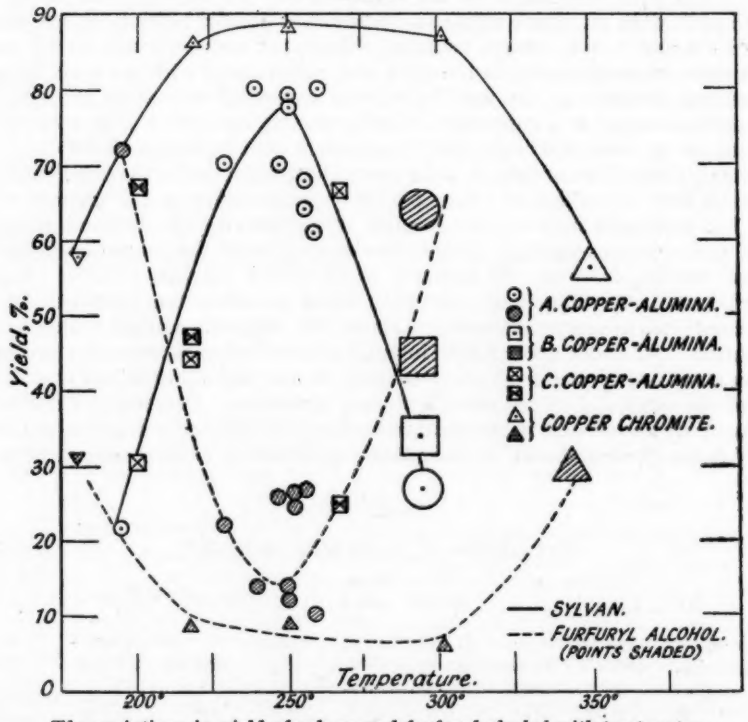
* The standard apparatus was used in all experiments except S.270, for which the jacket apparatus was used.

maximum temperature of about 400°. The peak temperature reached during such treatment is important since the alloy containing 55% of copper melts at 590°. A catalyst which has been worked at such temperatures shows obvious signs of fusion and is rendered permanently inactive.

The effect of temperature on the relative yields of sylvan and furfuryl alcohol was also examined

with the three Cu–Al_2O_3 catalysts A, B, and C. The results are shown graphically in Fig. 5. The hydrogenations were carried out under similar conditions of space velocity and hydrogen : furfuraldehyde ratio to those of Table II. To facilitate the temperature control in the lower range around 200° the jacketed apparatus with decahydronaphthalene (b. p. 190°) as temperature-control liquid was used in these experiments. The results closely resemble those of the alloy catalyst. At around 250° sylvan is formed in high yield, but at 200° furfuryl alcohol is the major product. In the region of 300° fairly rapid catalyst deterioration occurs, and with it a change from sylvan to furfuryl alcohol as the major product. The effect of temperature on pass conversion is shown in Fig. 6. At 200° conversion is not quite complete at a space velocity of 0·27 hr.$^{-1}$ (S.86) and falls from 80 to 48% (S.101) with an increase in space velocity to 0·66 hr.$^{-1}$, showing catalyst activity to be the limiting factor. At 250° and the normal space velocity of about 0·2 hr.$^{-1}$, conversion is practically complete. In the region of 300° the catalyst activity

FIG. 5.



The variations in yield of sylvan and furfuryl alcohol with temperature.

falls away progressively, so the pass conversion depends on the duration of the experiment. Catalysts which have deteriorated in this way may be restored in activity by treatment with air at about 400°, followed by reduction in hydrogen.

The variation in the ratio of sylvan to furfuryl alcohol with temperature is very similar for both the alloy and copper–alumina catalysts. The behaviour of the copper chromite catalyst is qualitatively similar. It is, however, very much less sensitive to temperature variations with regard both to the relative yields of furfuryl alcohol and sylvan and to the onset of deterioration.

The results for this catalyst, given in Table III, show sylvan to be the main product at both 250° and 300°. Even around 200° sylvan is still formed in high yield. A significant increase in the yield of furfuryl alcohol was obtained only by working at even lower temperatures, achieved by substituting furfuraldehyde (b. p. 162°) in the jacket for decahydronaphthalene as temperature-control liquid. In the higher temperature range, the onset of catalyst deterioration with the accompanying formation of furfuryl alcohol occurred only at temperatures near 350°. The results given by the copper chromite catalyst are included in Fig. 5.

(3) *The Effect of Alkalising the Catalyst on the Ratio of Sylvan to Furfuryl Alcohol.*—At temperatures around 250° different preparations of alkali-precipitated copper catalysts gave sometimes

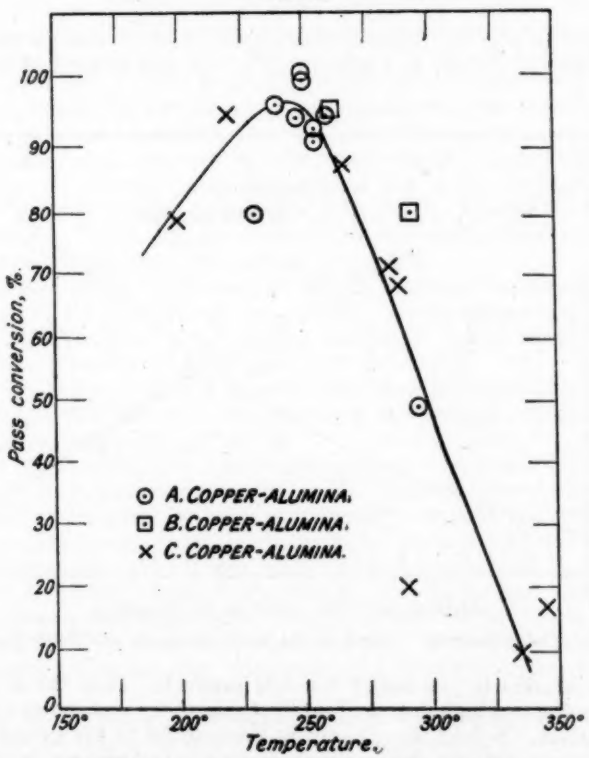
TABLE III.

*Examination of copper chromite catalyst.**

Expt. No.	Liquid space velocity ($hr.^{-1}$).	Temp.	Molar ratio H_2/aldehyde.	Duration of expt. (hrs.).	Pass conv. (%).	Yield, %. Sylvan.	Furfuryl alcohol.	Remarks.
S.272	0·19	178°	5·8	4·75	97	58	33	Furfuraldehyde as control liquid.
S.267	0·22	217	4·8	5·5	92·7	85	7	Decahydronaphthalene as control.
S.264	0·13	250	7·8	5·5	99	87	7	
S.276	0·13	301	6·2	4·5	98	87	5	
S.277	0·17	346	4·6	5·5	48	55	30	

* Jacketed tube apparatus used in first two experiments, and standard apparatus in last three.

FIG. 6.



The variation of pass conversion with temperature.

furfuryl alcohol and sometimes sylvan as the main product. It was considered that this might arise from a variation in the extent of washing of the precipitate, an appreciable amount of alkali being left in the final catalyst in some cases. To test this view, alkali additions were made to a 55% copper alloy catalyst. The results given in Table IV show the presence of alkali markedly to affect the course of the hydrogenation reaction.

Simple immersion of the activated alloy in sodium carbonate solution gave on hydrogenation a mixture of sylvan and furfuryl alcohol, and an almost complete change in the course of the action was achieved only by immersion under reduced pressure, to remove occluded gases. As the amount of alkali added under these conditions is not readily assessed, the A type $Cu–Al_2O_3$ was modified by successively increasing additions of sodium carbonate. This was accomplished by adding an alkaline solution of the requisite concentration to the pellets of volume such that complete absorption occurred, drying them, and then charging them into the catalyst tube. In this way catalysts containing 0·5, 2·5, 4, and 5% of Na_2CO_3 were prepared and examined at space velocities of about 0·2 $hr.^{-1}$ and a temperature of about 250°. The results obtained

TABLE IV.

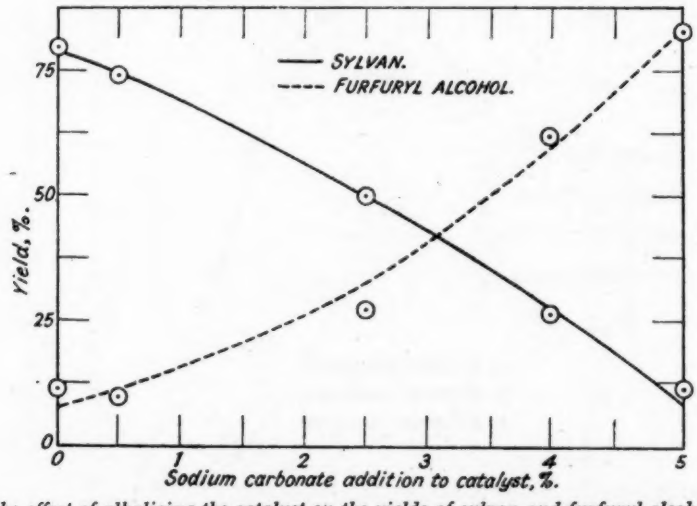
*Alkali addition to a copper alloy catalyst.**

Expt. No.	Liquid space velocity ($hr.^{-1}$).	Temp.	Molar ratio H_2/aldehyde.	Duration of expt. (hrs.).	Pass conv. (%).	Yield (%). Sylvan.	Yield (%). Furfuryl alcohol.	Alkalisation procedure.
S.185	0·16	253°	7·0	6·5	98·2	88	2	Catalyst only slightly water washed after caustic extraction.
S.186	0·20	254	5·8	6·5	96	32	58	Catalyst immersed in 5% aqueous Na_2CO_3 for 72 hours at room temp.
S.195	0·19	257	4·0	2·5	89	12	70	Catalyst immersed in boiling 5% Na_2CO_3 under reduced pressure.

* Standard type apparatus throughout.

are shown graphically in Fig. 7. Successive additions of alkali change the product from one consisting almost solely of sylvan, to a mixture of sylvan and furfuryl alcohol. At the higher

FIG. 7.



The effect of alkalising the catalyst on the yields of sylvan and furfuryl alcohol.

alkali additions the alcohol is practically the sole product. That the formation of furfuryl alcohol in this way is due to a high degree of catalyst selectivity was shown by the passage of the alcohol over the catalyst. Sylvan was present in the product to the extent of only 4·8%.

As with temperature variations, the copper chromite catalyst was much less sensitive to alkali addition than the alloy and copper–alumina type catalysts (see Table V).

TABLE V.

*Alkali addition to a copper chromite catalyst.**

Expt. No.	Liquid space velocity ($hr.^{-1}$).	Temp.	Molar ratio H_2/aldehyde.	Duration of expt. (hr.).	Pass conv. (%).	Yield (%). Sylvan.	Yield (%). Furfuryl alcohol.	Alkalisation.
S.259	0·16	242°	6·9	4·75	98	79	7	5% Na_2CO_3 added to catalyst before pelleting.
S.261	0·16	250	7·0	5·5	98	78	5	5% Na_2CO_3 added by impregnation of pellets.
S.262	0·16	295	6·7	6·0	99	88	3	
S.263	0·15	337	6·9	5·0	61·5	38	45	
S.279	0·18	252	6·5	6·0	99	66	23	20% Na_2CO_3
S.280	0·19	255	5·8	6·0	98	47	44	40% Na_2CO_3.

* Standard type apparatus.

The addition of 20% sodium carbonate gave some furfuryl alcohol in addition to sylvan. A striking transformation occurred during the experiment (S.280) in which the alkali content was increased to 40%. At the end of half the time projected for the experiment, during which sylvan was formed in excellent yield, a sudden change occurred and a homogeneous product was obtained containing 88·5% of furfuryl alcohol and 4·5% of furfuraldehyde. There is evidently a conditioning period for such a catalyst.

(4) *The Effect of the Presence of Carbon Monoxide in the Hydrogen on the Ratio of Sylvan to Furfuryl Alcohol.*—It was found that the presence of 7·2% of carbon monoxide in the reacting hydrogen left unchanged the formation of sylvan in high yield with a copper alloy catalyst at 250° and of furfuryl alcohol with an alkalised A type copper–alumina catalyst at 257°. These results are to be considered with the known strong adsorption of carbon monoxide on copper (Pease, *J. Amer. Chem. Soc.*, 1923, **45**, 2296) and its prevention at super-atmospheric pressure of the hydrogenation of aldehydes to alcohols in the Roelen reaction (U.S.P. 2,327,066). We conclude that under appropriate conditions both furfuraldehyde and furfuryl alcohol are strongly adsorbed on the catalyst surface.

(5) *Furfuryl Alcohol as Intermediate in the Formation of Sylvan.*—To show that furfuryl alcohol is an intermediate in the formation of sylvan it is necessary to work at incomplete conversion. The previous experiments show the alcohol to be formed in significant amount where conversion is incomplete owing either to a fall in catalyst activity with low operating temperature or to the incidence of catalyst deterioration at higher temperatures. Incomplete conversion may be achieved at the optimum temperature for the formation of sylvan either by using less than the stoicheiometric amount of hydrogen or by working at high space velocities. To investigate the former, a copper alloy catalyst was operated at 250° using hydrogen to furfuraldehyde molar ratios of 1·3 and 0·93 (Expt. Nos. S.273 and S.269). The pass conversions were 78% and 32%, respectively. While for the former the sylvan : furfuryl alcohol ratio was 2 : 1, equal amounts of each were formed at the lower conversion.

A pass conversion of 87% was obtained at 258° by working the copper alloy catalyst at the high space velocity of 1·15 hr.$^{-1}$ (Expt. No. S.281). Under these conditions furfuryl alcohol constituted 26% of the product. This result is similar to that obtained by working with less than the stoicheiometric amount of hydrogen (Expt. No. S.273).

The formation of furfuryl alcohol depends on the pass conversion in the manner to be expected of an intermediate product. Furthermore, the passage of the alcohol over the alloy catalyst gave sylvan in 86% yield (S.278).

(6) *Comparison of Furfuraldehyde with Acetone in Ease of Hydrogenolysis.*—Adkins recognises that carbonyl and hydroxymethyl groups are readily reducible to methylene and methyl groups only when attached to an aromatic nucleus (Gilman, " Organic Chemistry," 2nd Edition, I, 804, 820). This conclusion was based, in the main, on work carried out in the liquid phase at super-atmospheric pressure. That it also holds under the experimental conditions used in this work was demonstrated with acetone. Two experiments (S.164 and S.172) in which hydrogen and acetone were passed over a copper alloy catalyst at 249° and 246° gave liquid products which constituted 93·6 and 100% by weight of the acetone fed. *iso*Propanol and acetone dehydration products were present in the liquids. Evidently the extent of hydrogenolysis of acetone to propane is small.

(7) *Analysis of the Products of Hydrogenation of Furfuraldehyde.*—Sylvan and furfuryl alcohol, prepared in the course of this work, were redistilled to give samples for analysis (see

Property.	Material. Sylvan.	Furfuryl alcohol.
$d_4^{20°}$	0·9168	1·129
$n_D^{20°}$	1·4340	1·4846
B. p.	63—64°	—
H_2O content, %	0·1	0·43

Table). The unsaturation of the alcohol was measured with the pyridine sulphate–bromine reagent (Found : 304 g. bromine/100 g. Calc. for $C_5H_6O_2$: 325 g.).

Small amounts of pentanone-2 formed in some of the experiments were bulked together. The once-distilled material had $d_4^{20°}$ 0·809; $n_D^{20°}$ 1·393. It reacted with hydroxylamine hydrochloride under pressure (Found : CO, 30·0. Calc. for $C_5H_{10}O$: CO, 32·5%) (Smith and Bryant, *J. Amer. Chem. Soc.*, 1935, **57**, 57).

(8) *General Discussion of Results.*—An interpretation of the results obtained in this work must account for the following facts : (*a*) The ease with which the carbonyl group in furfur-

aldehyde may be reduced to the methylene group. (*b*) The promotion of the formation of sylvan by chromium oxides and its suppression by the presence of alkali. (*c*) The probable formation of furfuryl alcohol as intermediate in the formation of sylvan. (*d*) The formation of furfuryl alcohol in the region of 200° and of sylvan at 250°. (*e*) The decline in catalyst activity when it is operated at temperatures of 300° or higher.

Observations related to some of those given above have been mentioned in the literature. Reduction of the carbonyl and the nitro-group by chemical means gives products whose nature depends on the acidity or alkalinity of the medium. Acid conditions result in complete removal of oxygen to give methylene and amino-groups. Reduction is less complete under alkaline conditions (Hickinbottom, " Reactions of Organic Compounds," Chaps. IV and VIII), thus qualitatively resembling item (*b*) above.

In the catalytic field the use of alkalised catalysts has received frequent mention in reactions involving the hydroxyl and the amino-group. Where an alcohol is a product or reactant the former group may be removed by a process of dehydration (3) or hydrogenolysis (4) :

$$R{\cdot}CH_2{\cdot}CH_2{\cdot}OH = R{\cdot}CH{:}CH_2 + H_2O \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

$$R{\cdot}OH + H_2 = RH + H_2O \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

The dehydrogenation of alcohols to aldehydes and ketones is accompanied by little olefin formation if alkalised catalysts are used (B.PP. 313,093, 318,124; U.S.PP. 1,895,528, 1,984,884). Conversely the yield of alcohol formed by hydrogenation of aldehydes or ketones is not decreased by dehydration if alkali is present (F.P. 671,705; U.S.P. 1,895,515). In addition to suppressing the dehydration of alcohols, addition of alkali can increase the rate of hydrogenation of aldehydes and ketones to alcohols (Delépine and Horeau, *Compt. rend.*, 1935, **201**, 1301; Reasenberg, Lieber, and Smith, *J. Amer. Chem. Soc.*, 1939, **61**, 384) and of phenols to *cyclo*hexanols (Armstrong and Hilditch, *Proc. Roy. Soc.*, 1922, **102**, *A*, 21; McLaren, " Microfilm Abstracts," University Microfilms, Ann Arbor, 1944, V, No. 2, 39). The hydrogenation of furfuraldehyde in the liquid phase at super-atmospheric pressure is of interest as the presence of alkali causes the reaction to go smoothly in stepwise fashion through furfuryl alcohol to tetrahydrofurfuryl alcohol (U.S.PP. 1,906,873, 2,082,025; and unpublished work). In the absence of alkali the hydrogenation rate is slow and the by-product formation large.

The addition of alkali to the chromite catalyst used in the hydrogenation of carbon monoxide improves the yield of alcohols higher than methanol (Morgan, Hardy, and Proctor, *J. Soc. Chem. Ind.*, 1932, **51**, 1T).

That the loss of a hydroxyl group by the mechanism of equation (4) may also be suppressed by the presence of alkali has been shown by Griffith (" Contact Catalysis," Oxford Univ. Press, 1936, 69) in the case of phenol.

The apparently unrelated observations by Wilson (*J.*, 1945, 55, 61) that the copper chromite catalyst which hydrogenated furfuraldehyde to sylvan in good yield also catalysed the dehydration of tetrahydrofurfuryl alcohol to dihydropyran do, in fact, show the similarity of the two reactions depicted by equations (3) and (4). In demonstrating this similarity we should compare the activity of the catalyst for the dehydration of furfuryl alcohol with its ability to hydrogenolyse this alcohol to sylvan. For simplicity we have, however, examined the behaviour of the catalysts used in this work with *iso*propanol. The extent of its dehydration to propylene (ΔH = 16,200 cals.) would be expected to be large with those catalysts that favour sylvan formation. The formation of acetone by dehydrogenation (ΔH = 13,700 cals.) is to be expected with those catalysts that favour furfuryl alcohol formation. The results of these experiments carried out at 350° and a space velocity of 10 hr.$^{-1}$ are given in Table VI. Only 10 c.c. of catalyst were used to give approximately isothermal conditions, and the high space velocity was chosen so as to give incomplete conversion. These conditions tend to minimise effects due to the different activation energies of the dehydration and dehydrogenation reactions. The amounts of acetone and propylene formed are expressed by pass yield, *i.e.*, pass conversion × yield.

The effect of alkalisation in suppressing the dehydration of *iso*propanol is evident from the results given in Table VI. The alkalised copper chromite catalyst, however, shows exceptional behaviour in that it suppresses the dehydration of *iso*propanol while catalysing the hydrogenolysis of furfuraldehyde. This observation is probably connected with the relative ease of dehydration of *iso*propanol and furfuryl alcohol, the former occurring the less readily (cf. Storch, *J. Amer. Chem. Soc.*, 1935, **57**, 1395).

The use of alkali in the hydrogenation of compounds containing the amino-group includes the hydrogenation of nitrogen to ammonia (Larson and Brooks, *Ind. Eng. Chem.*, 1926, **18**,

TABLE VI.

The catalysed dehydration and dehydrogenation of isopropanol.

Exp. No.	Catalyst.	Product (pass yield, %). Acetone.	Propylene.
D.3	A copper–alumina	65·5	20·1
D.9	do. + 5% Na_2CO_3	11·5	1·6
D.11	Copper chromite	39·8	18·8
D.5	do. + 5% Na_2CO_3	55·2	1·8
D.1	Cu–Al alloy (20% Al removed)	65·5	4·1
D.7	do. + Na_2CO_3	29·0	1·7

1305; Almquist and Crittenden, *ibid.*, p. 1307; D.R.-P. 249,447; U.S.P. 1,667,322) and of aromatic amines to the alicyclic derivatives (Winans, *Ind. Eng. Chem.*, 1940, **32**, 1215; U.S.P. 1,927,130).

The rate of hydrogenation of nitrobenzene in the liquid phase is decreased by the presence of alkali (Reasenberg, Lieber, and Smith, *J. Amer. Chem. Soc.*, 1939, **61**, 384).

With regard to (*b*), Baljassny (*Ukrain. Akad. Nauk. Zapiski Inst. Khem.*, 1935, **2**, 175) has found that, whereas acetophenone may be hydrogenated with a copper catalyst at 250°, the reaction stops completely at 284—289°.

The intermediate formation of furfuryl alcohol, (*c*), is not in agreement with the theory advanced by Farkas and Farkas (*J. Amer. Chem. Soc.*, 1939, **61**, 1336) as a result of their work on the hydrogenation of acetone with a palladium catalyst at room temperature.

(9) *A Theory of Catalytic Action.*—In formulating a theory of catalysis to account for the observations in this work we have made the following assumptions. (*a*) Heterogeneous reactions frequently involve the formation, as intermediates, of radicals or radical ions. (*b*) The radicals and radical ions possess the relative stability accorded them in homogeneous reactions. (*c*) The behaviour of the radicals will be the same in heterogeneous as in homogeneous reactions.

It seems unnecessary under normal catalytic conditions to postulate the existence of radicals having an independent existence in the addition of hydrogen to a multiple bond (Vavon, *Bull. Soc. chim.*, 1936, **3**, 1021; Farkas, *Trans. Faraday Soc.*, 1939, **35**, 906). It is assumed that independent radicals exist where the addition or removal of a univalent atom or group is concerned as, *e.g.*, where the addition of a hydrogen atom is required to complete the hydrogenation (cf. Ingold and Burton, *J.*, 1929, 2022). Whether the fragment exists as a free radical (R), carbonium ion (R^+), or carbanion (R^-), as shown in equations (5) and (6), will depend on the relative stability of these radicals as well as the ability of the catalyst represented by M to provide or remove electrons:

$$R + M = R^+ + M^- \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

$$R + M^- = R^- + M \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

In this way we regard the catalyst as an electron donor or acceptor, *i.e.*, as basic or acidic in the Lewis sense. Any additions to the catalyst which decrease the availability of electrons, *i.e.*, its acidity, will make the existence of a carbonium ion less probable. Furthermore, an increase in temperature will aid the removal of electrons from the catalyst and tend to lead to the formation of carbanions.

On this basis a series of reactions can be set up to represent the hydrogenation of furfuraldehyde to sylvan and furfuryl alcohol. In the following equations we have used the symbol ψ to represent the furyl radical in which the substituent is in the 2-position, and M to represent the catalyst.

$$\psi\cdot CHO + H_2 + M = \psi\cdot CH_2\cdot OH + M \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

$$\psi\cdot CH_2\cdot OH + H + M = \psi\cdot \overset{+}{C}H_2 + H_2O + \overset{-}{M} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

$$\psi\cdot CH_2 + \psi\cdot CH_2\cdot OH + M = \psi\cdot CH_3 + \psi\cdot CH_2O + M \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

$$\downarrow$$

$$\psi\cdot CHO + H$$

The primary step comprises the formation of furfuryl alcohol by simple addition of hydrogen as in equation (7). Reaction (8), which involves the loss of a hydroxyl group with the formation of a carbonium ion, we regard as an essential step in both dehydration and hydrogenolysis reactions (Hammett, " Physical Organic Chemistry," 1940, Chap. X). In the alkanol series this ion will be relatively unstable, and a breakdown to an olefin with loss of a hydrogen atom will readily occur. The furfuryl radical, however, will be stabilised by resonance and consequently

have a relatively long residence time on the catalyst, during which it will acquire a hydrogen atom to form sylvan.

As is to be expected, hydrogenolysis of tetrahydrofurfuryl alcohol which is much less stabilised by resonance does not, in fact, give tetrahydrosylvan (unpublished work). It seems probable that an appreciable proportion of the hydrogen required for this step is provided by adsorbed furfuryl alcohol molecules as represented by equation (9). A deficiency of hydrogen on a catalyst surface is probable in hydrogenations at atmospheric pressure, more especially where the reaction is carried out in the liquid phase.

The hydrogen atoms of adsorbed alcohol molecules are known to exchange readily (Farkas, *Trans. Faraday Soc.*, 1937, **33**, 678). The hydrogen-transfer reaction represented by equation (9) may most simply be regarded as involving a free furfuryl radical formed by the reverse of reaction (5) (Waters, *J.*, 1946, 409; Hey, *Nature*, 1945, **156**, 36). That the dehydration of furfuryl alcohol does, in fact, give sylvan and furfuraldehyde by a disproportionation reaction similar to (9) has been shown by Paul (*Bull. Soc. chim.*, 1935, **2**, 2220):

$$2\psi\cdot CH_2\cdot OH = \psi\cdot CH_3 + \psi\cdot CHO + H_2O \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

Reaction (8) involving an electron transfer is regarded as a rate-determining one. The presence of chromium oxides will confer greater oxidising power or electron-acceptor characteristics to the catalyst and consequently make reaction (8) more likely. Conversely, alkali will increase the electron-donor characteristics of the catalyst and reduce the rate of the carbonium-ion formation. In these circumstances the alcohol formed will tend to be desorbed from the catalyst. The increased rate at which carbonyl compounds are hydrogenated by alkali addition in the liquid phase may be due to the increased catalyst area made available in this way.

The decreased effectiveness of alkali addition with copper chromite catalysts may be accounted for by the counterbalancing action of the chromium oxides. Conversely, we would expect the effects produced by alkalising a catalyst to be minimised by addition of chromium oxides. This prediction has, in fact, been demonstrated experimentally for the dehydration of ethanol with an alumina catalyst at 350°. The reduction in pass conversion arising from the presence of 2% of sodium carbonate on the alumina is practically eliminated by the subsequent addition of 2% of chromium sesquioxide.

We account for the change in the main product from furfuryl alcohol to sylvan with rise in temperature by the rate-determining nature of reaction (8). The fall in activity observed by operating at even higher temperatures is due to the accumulation on the catalyst surface of non-volatile material of high molecular weight, presumably formed by the interaction of free radicals or ions with the furyl nucleus (Hammett, *op. cit.*, pp. 307, 373; Hey, *loc. cit.*). Such condensation reactions are particularly evident where stabilisation of the intermediates by resonance is possible. Such an explanation may suitably account for the deterioration in catalyst activity observed by Baljassny during his hydrogenation of acetophenone.

It is hoped to publish an account of the implications of this theory to a wide variety of catalytic reactions.

Some of the work described in this paper has formed the subject of patent applications.

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203. *The Preparation, Properties, and Chlorination Products of Carbon Diselenide.*

By D. J. G. IVES, R. W. PITTMAN, and W. WARDLAW.

The action of methylene chloride vapour on heated selenium readily provides a good yield of carbon diselenide, which thus becomes accessible in considerable quantities for the first time. The vapour pressure of pure carbon diselenide has been measured over a range of temperatures and its behaviour with various reagents and solvents has been given preliminary study. It reacts vigorously with chlorine, giving a variety of products, of which selenium tetrachloride, *perchloromethylselenol*, *hexachlorodimethyl selenide* and *diselenide* have been isolated and characterised. Attempts to prepare selenocarbonyl chloride have not been successful.

THE only practical method hitherto available for the preparation of carbon diselenide depends on the interaction of hydrogen selenide with carbon tetrachloride in a hot tube (Grimm and Metzger, *Ber.*, 1936, **69**, 1356), but, contrary to the statement of these authors, this has been found to give an exceedingly poor yield of diselenide dissolved in excess of carbon tetrachloride, with which it forms an azeotrope. It has been found that methylene chloride vapour reacts with molten selenium with copious production of carbon diselenide, which has thus been prepared in the pure state in considerable quantities. It possesses interesting physical and chemical properties and presents a number of chemical problems which call for further investigation.

Methylene chloride vapour, carried in a stream of nitrogen, begins to react with molten selenium at 500° and produces carbon diselenide smoothly and rapidly at 550—600°. The deposition of carbon in the reaction zone tends to slow down and eventually stop the reaction, but this can be avoided by arranging for the supply of selenium in small quantities at a time to the reaction system. Copious evolution of hydrogen chloride occurs and some selenium is lost as a red, particulate cloud carried over in the gas stream : this difficulty may be partly obviated by the use of a fractionating column kept at about 200°. In a laboratory apparatus designed to meet these difficulties, the best yield of pure diselenide was 52% of the selenium used, without allowance for the considerable amounts of the element which should be easily recoverable from the reaction residues. In the routine preparation, however, a simpler apparatus giving a rather lower yield was found to be advantageous. Attempts to carry out the reaction solely in the vapour phase were unsuccessful, and the impression was gained that it occurs on the surface of liquid selenium.

Other hot-tube experiments of similar type gave no significant results. Methylene chloride gave no carbon disulphide with sulphur at 420° : carbonisation occurred and small amounts of hydrogen sulphide and hydrogen chloride were produced. No carbon sulphoselenide was formed by the interaction of methylene chloride with a mixture of selenium and ferrous sulphide at 425—560°, or by the action of methylene chloride and sulphur vapours on selenium at 500° : small amounts of carbon diselenide were produced in each case. Carbon ditelluride was not produced by the action of methylene chloride on tellurium at 450—680°. Methyl chloride with selenium at 400—550°, in addition to hydrogen selenide and hydrogen chloride, gave traces of a foul-smelling, lachrymatory, yellow liquid, which appeared to be different from carbon diselenide, but was not obtained in amount sufficient for characterisation.

Crude carbon diselenide was readily purified by distillation in steam, followed by distillation under either atmospheric or reduced pressure. It is a bright yellow, non-inflammable, highly refractive liquid (Grimm and Metzger, *loc. cit.*, report $n_D^{20°}$ 1·845) which does not wet glass. It has an intolerable odour, causes nose and lung irritation and lachrymation, and has a slight irritant action on the skin. On standing, it darkens, becoming brown, then black and deposits dark polymerisation products : loss of material due to this amounts to about 1% per month. The following physical properties were determined, values in parentheses being those previously recorded by Grimm and Metzger (*loc. cit.*) : b. p. 125—126°/760 mm. (124°/760 mm.), m. p. (pentane thermometer) − 40° to − 45° (− 45·5°), $d_{4°}^{20°}$ 2·6824 (2·679), $d_{4°}^{25°}$ 2·6626. Vapour pressures of the pure diselenide were determined, using a " spoon guage " incorporated in a high-vacuum apparatus, care being taken to ensure the complete " outgassing " of the sample used and to avoid any possibility of decomposition of vapour during the usual sealing-off procedure. Manometric readings were corrected to 0°, sea-level, and latitude 45°. The results are shown in the table, together with vapour pressures calculated from the equation $\log_{10} P$ (mm.) = 7·9153 − 1987·4/T, where T is the absolute temperature.

Temp.	0·00°	5·07°	10·07°	15·07°	20·07°	25·06°	30·04°	35·04°	40·02°	50·01°
$P_{obs.}$, mm.	4·7	5·7	7·7	10·4	13·6	17·9	23·3	29·6	37·0	58·2
$P_{calc.}$, mm.	4·4	5·9	7·9	10·4	13·7	17·8	22·9	29·3	37·1	58·3

It will be seen that the vapour-pressure equation fits the experimental points with a mean deviation of ± 0·2 mm. and leads to an average latent heat of evaporation over this temperature range of 9092 cals./mole. Comparison with carbon disulphide has been made by Othmer's method (*Ind. Eng. Chem.*, 1940, **32**, 841), leading to an approximate latent heat of evaporation at the b. p. of 7855 cals./mole and an entropy of evaporation of 19·7 cals./deg./mole. Hildebrand's constant has been calculated as 28·5 (cf. carbon disulphide, 27·1).

Various observations have been made of the behaviour of carbon diselenide with solvents and reagents, in addition to those already recorded by Grimm and Metzger (*loc. cit.*). It is completely miscible with carbon tetrachloride, with which it forms a constant-boiling mixture

containing about 40% of the latter; it is also miscible in all proportions with carbon disulphide and toluene. These solvents appear to retard the polymerisation of the selenide. It is readily soluble in light petroleum (b. p. 60—80°), but in this case the polymerisation does not appear to be retarded. Medicinal paraffin dissolves carbon diselenide to about 25% by volume and the components show an upper critical solution temperature. The diselenide is very sparingly soluble in glacial acetic acid and also in ethanol, which appears to promote decomposition. It is insoluble in water and appears to suffer loss of stability under moist conditions: the upper aqueous layer rapidly becomes turbid. White phosphorus dissolves to a very large extent. Selenium oxychloride reacts violently with carbon diselenide, much elementary selenium being deposited with liberation of unidentified volatile products. Selenium monochloride reacts briskly after a period of induction, giving selenium and a volatile product of intolerable odour. Bromine reacts with a "quenching" sound, giving a clear red liquid which deposits a dark brown solid on standing. Dry hydrogen chloride has no apparent reaction and neither has the concentrated aqueous acid, from which the diselenide steam-distils on boiling. Concentrated nitric acid has little action in the cold, but destroys the diselenide on boiling, although the compound distils in the vapour of the boiling acid for a considerable time. Concentrated sulphuric acid has a more rapid action, but again unchanged selenide can be distilled from admixture for some time. Oleum produces rapid decomposition. Concentrated aqueous sodium hydroxide has little action in the cold, but dissolves carbon diselenide on heating, giving an orange solution. Alcoholic potash dissolves and destroys the diselenide rapidly and affords the best means of decontaminating apparatus which has contained it. Dry bleaching powder produces a vigorous exothermic reaction accompanied by the evolution of most aggressive vapours. It is apparent that there is a wide field of investigation still open in the chemistry of carbon diselenide, but the only reaction which opportunity has allowed us to study is that with chorine.

Chlorine is absorbed rapidly in large amounts by carbon diselenide, with evolution of much heat. A great variety of interesting products appears to be formed: bright red and yellow solids, white red and black sublimates, red, yellow, and green liquids. Some of these are very unstable; a yellow solid deliquescing rapidly in air, with evolution of pink fumes, provides a striking example. Simplification of this complex reaction was achieved by carrying out chlorination in carbon tetrachloride, in which selenium tetrachloride is sparingly soluble, removal of the latter product by filtration, removal of carbon tetrachloride by distillation, rapid washing of the residue with water, and high-vacuum distillation. Four products were thus characterised with reasonable certainty, the chief of which was selenium tetrachloride. The others were *perchloromethylselenol*, $CCl_3 \cdot SeCl$, a deep red liquid, b. p. 62°/23 mm., with a biting odour, fuming in air and hydrolysing fairly rapidly with water. *Hexachlorodimethyl selenide*, $(CCl_3)_2Se$, was obtained in small amount. It is a white, crystalline solid, m. p. 37°, with an odour resembling that of hexachloroethane. It is soluble in benzene and carbon tetrachloride, and is intermediate in volatility between the above selenol and *hexachlorodimethyl diselenide*, which was obtained in very small yield as a yellow oil, b. p. 126°/0·5 mm., with a camphoraceous odour and an irritant action on the skin. Further treatment with chlorine appears to convert the diselenide into the selenol and selenium tetrachloride.

It is remarkable that no success was achieved in obtaining selenocarbonyl chloride as a product of this chlorination reaction, and although high volatility would not be expected in this compound, it is noteworthy that a volatile selenium compound with a most aggressive and quite intolerable odour has been produced in a number of ways which might conceivably lead to this compound. Such a substance was present in the carbon tetrachloride distilled from the carbon diselenide chlorination mixture, was produced by the interaction of selenium monochloride with carbon diselenide and by the reaction of the latter with dry bleaching powder, and also by the reduction of perchloromethylselenol with anhydrous stannous chloride in carbon tetrachloride solution. The chlorination of selenoformaldehyde was also attempted as a source of selenocarbonyl chloride, but other products, not yet investigated, were produced in this reaction.

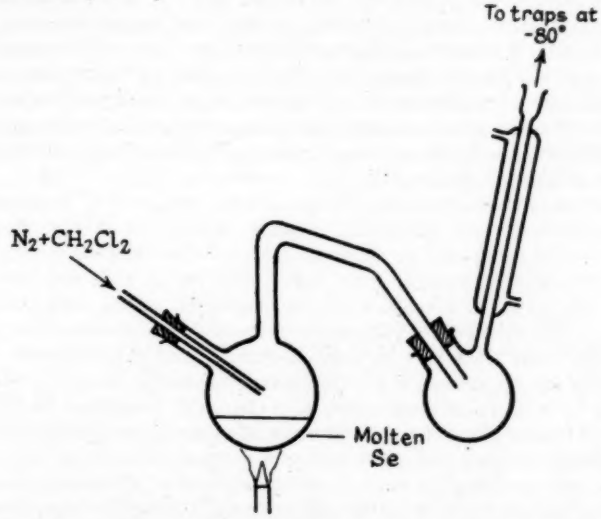
It is clear that much work remains to be done in this interesting field of selenium chemistry, but it is attended by the disadvantage of the rather toxic and highly disgusting nature of the products obtained.

Experimental.

Carbon Diselenide.—Various experimental conditions and types of apparatus indicated the desirability of removing the reaction products as rapidly as possible from the zone of reaction between methylene chloride and molten selenium in order to minimise the deposition of carbon. Too high a temperature

and too extensive a heated zone were also to be avoided from this point of view. These requirements, and the desirability of a reasonable production rate, made unavoidable the loss of considerable amounts of selenium in the form of red smoke, which could ultimately, however, be recovered. The simplest satisfactory apparatus consisted of a Pyrex retort, delivering into a receiver, as indicated in the figure. Methylene chloride vapour, provided by a vessel containing the liquid maintained at a suitable fixed temperature, was delivered above the surface of molten selenium in a stream of dry nitrogen. The crude product was steam-distilled directly from the receiver, separated from the aqueous layer, dried ($CaCl_2$), and, for purposes of the physical measurements, fractionated through a 30-cm. vacuum-jacketed Dufton column under reduced pressure (b. p. 46°/50 mm.) (Found: Se, by combustion, 92·77; by Kjeldahl, 92·96. Calc. for CSe_2: Se, 92·93%).

Chlorination of Carbon Diselenide.—Preliminary attempts at separation of the products of reaction indicated the importance of analyses for selenium and chlorine at frequent intervals. The most rapid and satisfactory methods were found to be as follows: for selenium, digestion with oleum and perhydrol (Kjeldahl), followed by dilution, reduction with sulphur dioxide and then with hydroxylamine hydrochloride, and gravimetric estimation as elementary selenium; for chlorine, treatment with sodium in liquid ammonia, followed, after evaporation of ammonia, by treatment with alcohol, boiling with dilute sulphuric acid, treatment with sulphur dioxide, further boiling, filtration, and precipitation with silver nitrate in the usual way.



The course of a chlorination experiment was as follows. Carbon diselenide (50 g.), dissolved in carbon tetrachloride (300 c.c.) in a 1-l. flask fitted with a mechanical stirrer and reflux condenser, was treated with dry chlorine until an increase in weight of 81 g. was reached (approx. 4 moles of Cl_2). A large precipitate of whitish solid was produced, together with red and yellow sublimates. The reaction mixture was set aside for two days, and darkening occurred. The solid was removed by filtration, washed at the pump with carbon tetrachloride, and proved to be selenium tetrachloride (Found: Se, 35·9; Cl, 64·0. Calc. for $SeCl_4$: Se, 35·8; Cl, 64·2%). The filtrate was carefully fractionated, a vacuum-jacketed Dufton column being used with controlled reflux-ratio head. The first distillate, consisting mainly of carbon tetrachloride, was yellow-brown, contained considerable amounts of selenium, and had an intolerable odour reminiscent of carbonyl chloride, but no definite compound could be isolated from it. The residue from this fraction was completely distilled at 200 mm. The second distillate was shaken with water, separated, dried ($CaCl_2$), and redistilled in vacuum. The first fraction consisted of *perchloromethylselenol* (17 g.), b. p. 62°/23 mm. (Found: Se, 33·75; Cl, 60·7; *M*, cryoscopic, in C_6H_6, 247. CCl_3·SeCl requires Se, 33·9; Cl, 60·9%; *M*, 233). Further distillation yielded a pale yellow oil which solidified in the condenser. This and the residue in the distillation flask were removed and examined separately. The liquid residue was removed to a smaller apparatus and redistilled (b. p. 124—129°/2 mm.). Admission of air to the apparatus caused oxidation, with production of green and red substances. In view of this difficulty and the low volatility of the substance, redistillation was effected in a high vacuum. A small homogeneous fraction consisting of *hexachlorodimethyl diselenide* was obtained (Found: Se, 40·2; Cl, 53·8; *M*, cryoscopic in C_6H_6, 392. $C_2Cl_6Se_2$ requires Se, 40·0; Cl, 53·9%; *M*, 395). The solid condensate from the previous distillation was recovered by dissolving in carbon tetrachloride. The solvent was removed, and the residue sublimed in a high vacuum, giving a small yield of *hexachlorodimethyl selenide* (Found: Se, 25·3; Cl, 67·4; *M*, cryoscopic in C_6H_6, 317. C_2Cl_6Se requires Se, 25·0; Cl, 67·4%; *M*, 316).

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204. *The Relation of Yttrium to the Lanthanons: A Study of Molecular Volumes.*

By Joseph K. Marsh.

When yttrium concentrates near samarium or neodymium in the lanthanon series, molecular and not ionic states are believed to be involved. The molecular volume of yttrium acetylacetone is found to approximate to that of neodymium, and to be larger than those of the lanthanons similar to yttrium in ionic size. Nevertheless, yttrium basic nitrate and ferricyanide were found to give molecular volumes indicating a polar crystalline state, though they accumulate at the position of No. 61 on fractionation. The basic nitrate will be un-ionised in nitrate solution, and triply ionised ferricyanide is unlikely to reach the solubility product with $Y^{\cdots}$ or $Ln^{\cdots}$. The reaction to form these ferricyanides is therefore believed to be molecular in character, thus accounting for the behaviour of yttrium. This reasoning can be extended to other slightly soluble yttrium salts with multivalent anions (*e.g.*, phosphate, chromate, and ferrocyanide) showing similar behaviour.

In a previous communication (Marsh, this vol., p. 118) the suggestion was made that yttrium on passing from the ionic to the covalent state underwent a relatively larger increase in size on comparison with the lanthanon elements. For instance, yttrium and holmium ions are approximately of the same size, but sometimes yttrium shows behaviour indicating a resemblance to neodymium and samarium, which elements have larger ions than holmium. Certain sparingly soluble and basic salts incline to show yttrium associating with elements larger than holmium. A reason for this behaviour is now sought.

It is firmly established that a progressive fall in ionic radius with increasing atomic number occurs between lanthanum and lutecium. This is found by *X*-ray determination of the crystal-lattice size, and is confirmed by determination of the molecular volumes of the sulphate octahydrates (von Hevesy, *Z. anorg. Chem.*, 1925, **147**, 217; **150**, 68), though in both these instances the first two or three members of the rare-earth group lack isomorphism with the remainder. In the oxide series the yttrium ion falls in size between those of dysprosium and holmium, and in the sulphate series between holmium and erbium ions. The latter is the position usually taken by yttrium in a fractional crystallisation series, indicating an important correlation between ionic and molecular sizes and chemical properties in the lanthanon series. Generally, yttrium is isomorphous with holmium and erbium, but exceptions are known. For example, the 2-bromo-5-nitrobenzenesulphonates of yttrium crystallise with $10H_2O$ similarly to those of samarium and gadolinium and in contrast to the dodecahydrates of erbium and ytterbium. Direct evidence of yttrium having at times a larger volume than holmium is now sought by measurement of molecular volumes: it has already been reported in the case of the atomic volumes of the metals (Bommer and Hohmann, *Z. anorg. Chem.*, 1939, **241**, 268). The crystalline basic nitrates and the ferricyanides have been examined throughout a representative series of earths. These are two good examples of salts by the formation of which rapid accumulation of yttrium with neodymium and samarium, and separation from the "yttrium earths", is brought about, but in both instances the molecular volume of the yttrium salt proved to have a value which placed yttrium in sequence in the usual ionic position among the other elements, *i.e.*, near to holmium. The crystals must therefore be regarded as polar in type. The acetylacetones, however, gave evidence that this covalent yttrium compound has in fact a larger molecular volume than that of the usual associates of yttrium in its ionic state.

The basic nitrates are obtained by crystallisation from hot concentrated nitrate solutions. They are decomposed by water, but in nitrate solution they appear to be stabilised by suppression of ionisation by a common-ion effect, on removal of which they hydrolyse. They may be regarded as existing in a non-ionising solvent only. If, then, they exist in solution in a non-ionised form, it is not surprising to find that the solubility of yttrium basic nitrate has a value interpolating in the lanthanon series at the position of No. 61, the same as is found in the case of the atomic volume, or the acetylacetone molecular volume. We must then postulate a transition from a non-ionic to an ionic state upon crystallisation, based on the evidence of the crystal molecular volumes. The precipitate produced by boiling a nitrate solution with sodium nitrite, being chiefly the basic nitrate $Y_6C_{14}(NO_3)_4.17H_2O$ (Fogg and James, *J. Amer. Chem. Soc.*, 1922, **44**, 397), appears to be a similar case to the basic nitrate $Y_6O_5(NO_3)_8.20H_2O$ produced by crystallisation (James and Pratt, *ibid.*, 1910, **32**, 873).

In the case of the ferricyanides, high concentrations of potassium ferricyanide and up to 200 g./l. of yttrium oxide in the form of chloride can be brought together in cold solution without any precipitate forming, yet the solubility of $YFe(CN)_6$ at 20° is represented by only

0·602 g./l. of Y_2O_3 (Prandtl and Mohr, *Z. anorg. Chem.*, 1938, **236**, 243). Seeding is ineffective in producing a precipitate. Indeed, the seed may dissolve, but on gentle warming a precipitate forms slowly, which has a molecular volume indicative of an ionic state of yttrium. An irreversible reaction takes place, since the precipitate will not redissolve appreciably on cooling. The formation of yttrium ferricyanide according to the simple equation $Y^{\cdots} + 3Cl^- + 3K^+ + Fe(CN)_6^{---} = YFe(CN)_6 + 3KCl$ cannot be expected to take place, since triple ionisation of ferricyanic acid is necessitated. Thus, in general, it will be seen that molecular reactions may be expected where the alternative involves the existence of a multivalent anion or the production of a series of unknown intermediates. Ferrocyanide, chromate, and phosphate are other examples of salts of yttrium showing closer resemblance to neodymium than to holmium in fractionations. All are compounds having low solubilities and are salts of multivalent acids incapable of complete ionisation.

A series of acetate molecular volumes have been measured, and as anticipated yttrium takes an ionic position in the series. The densities and molecular volumes of the four series of salts examined are presented in Table I. The values for the acetylacetones might be doubled, since the molecules are known to be double in solution. No high degree of accuracy for the molecular volume determinations can be claimed for these last compounds, but the results are sufficiently reliable to prove the point that the value for yttrium does not lie in the sequence close to those of the other yttrium earths, but is larger and more nearly equal to that of neodymium. The fused acetylacetone compounds were usually somewhat basic as indicated by high oxide contents on ignition. The densities found must therefore tend to be high and the molecular volumes low. For Table I, data have been selected from the italicised data of Table II,

TABLE I.

Densities.

	La.	Nd.	Sm.	Gd.	Dy.	Y.	Er.	Yb.
Acetates	—	1·885	1·942	1·990	2·042	1·689	2·075	2·142
Basic nitrates	—	—	2·940	3·045	3·159	2·431	3·223	3·326
Ferricyanides	2·044	2·110	2·179	2·243	—	1·937	2·348	2·410
Acetylacetones	1·542	1·618	1·651	1·678	1·709	1·403	—	1·748

Molecular volumes.

Acetates	—	208·7	205·8	205·0	201·6	200·4	199·9	197·1
Basic nitrates	—	—	634	617	605	605	602	594
Ferricyanides	207	203	199	197	—	193	192	190
Acetylacetones	283	273	271	271	269	275	—	269

TABLE II.

Acetylacetones.

	Density.			Oxide, %.				Molecular volume.				Oxide, %, in excess.
	1.	2.	3.	1.	2.	3.	Calc.	1.	2.	3.	Best.	
La ...	*1·536*	*1·549*	—	*36·75*	*35·82*	—	37·34	*284·0*	*281·6*	—	283	−2·9
Nd ...	*1·618*	1·664	1·694	*39·05*	40·80	41·34	38·11	*273·3*	265·4	260·5	273	2·5
Sm ...	*1·636*	*1·666*	1·689	*40·92*	*40·43*	42·22	38·95	*273·7*	*268·8*	265·1	271	5·6
Gd ...	*1·676*	1·712	—	*42·33*	43·62	—	39·82	*270·7*	265·4	—	271	6·3
Dy ...	*1·709*	1·726	—	*42·94*	45·25	—	40·55	*269·1*	266·5	—	269	5·9
Y ...	*1·393*	*1·400*	*1·416*	*30·83*	*29·85*	*31·47*	29·23	*277·1*	*275·2*	*272·7*	275	5·1
Yb ...	*1·740*	*1·746*	*1·759*	*43·58*	*43·60*	*41·28*	41·90	*270·5*	*269·5*	*267·5*	269	2·2

sometimes by averaging, but more often by selection of the value relating to the acetylacetone sample which showed the nearest approach to theoretical oxide content. A fairly constant density increment of 0·03 between even-numbered elements from neodymium to dysprosium inclusive is found, and the excess oxide, except in the case of neodymium but with the addition of yttrium, is also fairly constant, so that this sequence of elements is comparable, and they lend mutual support. It was found that lanthanum acetylacetone was slightly volatile. Its true oxide content cannot therefore be determined by ignition and the low contents recorded in Table II are suspect. On the other hand, the low densities for the acetylacetone leading to an unexpectedly high value for the molecular volume are consistent with the presence of excess acetylacetone, but the melts were not gummy, as would be expected in that event, but quite vitreous. This in other instances accompanied deficient acetylacetone.

If we examine the molecular volumes of isomorphous compounds of neodymium and ytterbium, we find the values for the latter smaller than those of the former by the following percentages: sulphates 7·0, ferricyanides 6·5, acetates 5·6, ethyl sulphates 3·0. The fall in the case of the acetylacetone compounds appears to be under 2%.

Experimental.

Densities.—In the case of the acetates, suspension of crystals in mixtures of chloroform and bromoform and determination of the density of the liquid by a Westphal balance proved very satisfactory. With basic nitrates and ferricyanides, determinations of the loss of weight in chloroform was more satisfactory, and the acetylacetones were weighed in water. A platinum bucket of 2 ml. capacity and about 0·5 g. of substance were used in these three cases. The accuracy of the method depended chiefly on the proper release of air bubbles before weighing in liquid.

Acetates, $E(C_2H_3O_2)_3,4H_2O$.—The neodymium salt was prepared by evaporation of a solution in a desiccator. It is rather efflorescent, but large crystals may be grown. The other acetates crystallised readily from warm neutral solutions, and are stable.

Basic Nitrates, $E_6O_5(NO_3)_8,20H_2O$ (James and Pratt, *loc. cit.*).—The normal slightly acid nitrates were boiled to dryness and heated till some decomposition had occurred. The vitreous melts were then poured into cold water and gave clear hot solutions which deposited crystals overnight. It was found possible to prepare the samarium basic nitrate if only slight decomposition of the melt was permitted, for its range of stability is small. The melt was vitreous like the others. Neodymium gave no vitreous melt or basic nitrate crystals. The nitrate creamed at once when decomposition began.

The density of the erbium salt as given in Table I is an extrapolation from the experimental value using material containing 2% of yttrium. Only a very small sample of dysprosium basic nitrate was available, and the single determination of the molecular volume appears low. Other values are believed to be correct within $\pm$ 2. Three determinations for yttrium were within 1 part in 500.

Ferricyanides, $EFe(CN)_6,4H_2O$.—Neutral chloride solutions containing 100 g./l. of oxide were treated at 40—50° dropwise with cold saturated potassium ferricyanide with mechanical stirring and the precipitate which formed was collected, washed, and dried. The precipitates of samarium and gadolinium could not be obtained as coarsely crystalline as in the other cases. Prandtl and Mohr (*Z. anorg. Chem.*, 1938, **236**, 243; **237**, 160) found some variation in the amount of water of crystallisation in the different salts but apparently without loss of isomorphism: *e.g.*, for the lanthanum salt they found $4·5H_2O$, but the molecular volumes shown in Table I are calculated for $4H_2O$ in all cases.

Acetylacetone Compounds, $E[CH(CO·CH_3)_2]_3$.—Acetylacetone (3 g. in 10 ml. of alcohol) was added to an equivalent of lanthanon acetate in 50 ml. of cold water, and ammonia added dropwise with stirring, excess being avoided. The acetylacetone compound soon separated and was collected with suction. Especially in the case of ytterbium, acetylacetone washing appeared to decompose the precipitate. Washing was therefore omitted or kept to a minimum, but the products were well pressed on filter-paper and dried in a desiccator. Melting points were found to be close to known values without further purification.

Lanthanum acetylacetone. The precipitate appeared to be basic and did not give a clear melt unless one or two drops of acetylacetone were added before fusion; then clear melts giving a vitreous, pale amber solid were obtained.

Neodymium acetylacetone. This, m. p. 150—152°, like the lanthanum compound, appeared basic (Found: Nd_2O_3, 39·04. Calc.: Nd_2O_3, 38·11%) and failed to give a clear melt without additional acetylacetone.

Gadolinium acetylacetone. This compound, m. p. 140°, was likewise basic (Found: Gd_2O_3, 40·53. Calc.: Gd_2O_3, 39·83%). Unlike preparations previously reported it did not appear to contain any water of crystallisation (1 and 2 H_2O, Jantsch and Meyer, *Ber.*, 1920, **53**, 1594; 3 H_2O, Sarkar, *Bull. Soc. chim.*, 1926, **39**, 1390). If damp acetylacetones were heated to their m. p. they reacted with water to form the hydroxides and failed to give satisfactory melts.

Ytterbium acetylacetone. This had m. p. 114° but the melt was not clear. It did not gas at the m. p., as occurred with the higher-melting acetylacetones melting near the b. p. of free acetylacetone. It was not considered likely that satisfactory density determinations by weighing the finely crystalline compounds in water could be made, nor could organic liquids be used, since they have solvent action. Quantities of about 1 g. were therefore fused in an oil-bath in thin 10-mm. specimen tubes with, when necessary, the addition of one or two drops of acetylacetone to give clear melts. Loss of acetylacetone occurred at the m. p. Unless a slight loss did occur, the fused mass cooled to a stiff gum which would quickly crystallise if kneaded. But when slightly basic, a vitreous resin was obtained in one or more large pieces on breaking the tubes, and the densities of these pieces could be obtained with a fair degree of accuracy by weighing in water. There was, however, always some devitrification or hydroxide formation on the surface in contact with water, with loss in weight. The surface deposit was removed so far as possible after determining the density, and the percentage of oxide contained in the material was obtained by ignition. In some cases burning the oxide free from carbon was difficult. The char required to be broken down with a glass rod in the silica crucible before final ignition. Particular care was taken to obtain reliable data for yttrium. The three analyses are in satisfactory agreement but the third shows a high density and high oxide content and low molecular volume. The final figure adopted in Table II for the molecular volume of yttrium acetylacetone is therefore likely to be a little low.

Dr. A. S. Russell is thanked for permission to use this laboratory.

Dr. Lee's Laboratory, Christ Church, Oxford. [*Received, November 9th*, 1946.]

205. *The Preparation and Ultra-violet Light Absorption of Some Substituted Phenylpropenyl- and Styrylmethyl-carbinols and 1-Phenylbutadienes.*

By Ernest A. Braude, E. R. H. Jones, and E. S. Stern.

In connexion with kinetic studies on anionotropic rearrangements (see following paper), carbinols of the type $C_6H_4R{\cdot}CH(OH){\cdot}CH{:}CHMe$, where R = *o*-Me, *m*-Me, *p*-Me, *p*-F, *p*-Cl, *p*-Br and *p*-MeO, have been prepared by Grignard condensations of appropriate aromatic halides with crotonaldehyde. Quantitative conversions into the isomers $C_6H_4R{\cdot}CH{:}CH{\cdot}CH(OH)Me$ are effected by treatment with hydrochloric acid in aqueous dioxan. Dehydration of the carbinols by distillation from potassium hydrogen sulphate yields the dienes $C_6H_4R{\cdot}CH{:}CH{\cdot}CH{:}CH_2$, which are characterised by their adducts with maleic anhydride and with benzoquinone. The ultra-violet light absorption properties of the various compounds are discussed and provide evidence for the smaller polarisability of the phenyl nucleus as compared with the ethylenic bond.

The extension of the kinetic studies on anionotropic rearrangements carried out in these laboratories (cf. Braude and Jones, *J.*, 1946, 122, 128; Braude, Jones, and Stern, *ibid.*, p. 396) required the preparation of substituted phenylpropenylcarbinols (I) and of the isomeric styrylmethylcarbinols (II). Only the parent carbinols (I and II, R = H) have been described

$C_6H_4R{\cdot}CH(OH){\cdot}CH{:}CHMe$ (I.) $\qquad$ $C_6H_4R{\cdot}CH{:}CH{\cdot}CH(OH){\cdot}Me$ (II.)

hitherto. A number of substituted phenylvinylcarbinols have been prepared by Burton and Ingold (*J.*, 1928, 904) and Burton (*ibid.*, p. 1650), but the lower mobility of phenylvinyl- as compared with phenylpropenyl-carbinol (Braude, Jones, and Stern, *loc. cit.*) indicated that the vinylcarbinols would be less valuable for kinetic studies than their propenyl homologues.

The simplest route to phenylpropenylcarbinols is by the Grignard condensation of the appropriate aryl halides with crotonaldehyde. Qualitative data in the literature (cf. Runge in Schmidt, "Chemie in Einzeldarstellungen," Vol. 16, Part I, Stuttgart, 1932) indicate that the reactivity of aryl halides towards magnesium varies in the order ArCl < ArBr < ArI. Furthermore, it is said to be enhanced by methyl substituents, decreased by halogen and methoxyl substituents, and completely destroyed by substituents, such as the nitro-group, exerting only electron-attracting effects. The range of compounds accessible by this method is therefore limited. In the present work it was found that the bromotoluenes and *p*-bromofluorobenzene all reacted readily with magnesium in the presence of a small amount of ethyl bromide. *p*-Dibromobenzene and *p*-bromoanisole reacted somewhat less readily, while with *p*-dichlorobenzene the reaction was incomplete even after four days. With *p*-di-iodobenzene the metal slowly disappeared after prolonged treatment, but in contrast to the findings of Bruhat and Thomas (*Compt. rend.*, 1926, **183**, 297; cf. Mihailescu and Caragea, *Chem. Zentr.*, 1930, I, 2248) no significant yield of condensation product with crotonaldehyde could be obtained, some of the di-iodobenzene being recovered unchanged, together with iodobenzene, and intractable residues. Attempts to make *p*-bromonitrobenzene react with magnesium, using Grignard's technique (*Compt. rend.*, 1934, **198**, 625) of adding an equimolecular proportion of ethyl bromide simultaneously with the unreactive halide, only yielded unchanged starting material and small amounts of *pp'*-dibromo-azo- and -hydrazo-benzenes (cf. Werigo, *Annalen*, 1873, **165**, 190; Hepworth, *J.*, 1920, **117**, 1004; Slotta and Heller, *Ber.*, 1930, **63**, 3030). Again, the bromomagnesium derivative of *p*-bromophenol, though soluble in anisole at 100°, failed to react with magnesium.

The Grignard derivatives of the first eight halides mentioned were condensed with crotonaldehyde, special attention being paid to temperature control during the addition of the aldehyde and during the decomposition of the complex with ammonium chloride, in order to avoid the formation of the isomeric styryl derivatives. Thus, even in the preparation of the much less readily isomerised phenylvinylcarbinol, the product contains some cinnamyl alcohol unless the last two stages are carried out below 20°. It is known that, *vice versa*, cinnamylmagnesium chloride reacts partly in the form of phenylvinylcarbinylmagnesium chloride (Gilman and Harris, *J. Amer. Chem. Soc.*, 1927, **49**, 1825) and it may well be, therefore, that the Grignard derivatives themselves undergo some equilibration.

The substituted phenylpropenylcarbinols were isolated in good yields as viscous liquids or low-melting solids. In view of their ready isomerisation in the presence of acids, traces of the latter were excluded by drying over, and distilling from traces of, potassium carbonate.

In the absence of these precautions, some of the rearranged styrylmethylcarbinols and phenylbutadienes are invariably produced, and considerable resinification occurs. This is particularly noticeable with the highly mobile *p*-anisylpropenylcarbinol.

Rearrangement of the phenylpropenylcarbinols was effected by treatment with hydrochloric acid in aqueous dioxan, the corresponding styryl isomers being obtained in almost quantitative yields. In aqueous alcohol a mixture of the carbinols and their ethyl ethers is produced (cf. Braude, Jones, and Stern, *loc. cit.*) and kinetic data (see following paper) indicate that with the chloro- and bromo-carbinols some etherification occurs before, as well as during, rearrangement.

Treatment of the phenylpropenylcarbinols with α-naphthyl *iso*cyanate in the absence of solvent gave the naphthylurethanes of the corresponding styrylmethylcarbinols. In petrol solution and in the presence of traces of pyridine, mixtures of the isomerised and unisomerised naphthylurethanes were obtained. The latter could not be isolated pure, however, as they readily rearrange to the former on attempted recrystallisation. The two types of derivatives are distinguished by their characteristic ultra-violet light absorption (see below).

It has long been known that methylstyrylcarbinol can readily be dehydrated to phenylbutadiene (Klages, *Ber.*, 1902, **35**, 2650); in fact, early workers experienced considerable difficulty in obtaining the pure carbinol by the condensation of cinnamaldehyde with methylmagnesium iodide because they omitted to eliminate traces of iodides and of acids which act as dehydration catalysts. In the present work, the rearrangement and subsequent dehydration of the phenylpropenylcarbinols were conveniently carried out in one stage by means of potassium hydrogen sulphate. The carbinol together with about one-tenth of its weight of sulphate is preheated to 80—100° at 10^{-3} mm. until the vigorous rearrangement reaction sets in (5—30 mins.). In the case of the *p*-anisyl- and *p*-bromophenyl-propenylcarbinols the solid styryl isomers are deposited on the sides of the vessel. The temperature is then raised and the phenylbutadiene distils over as the dehydration proceeds. The ease of dehydration appears to vary in the same order as that of the isomerisation of the parent carbinols. The substituted phenylbutadienes are highly refractive liquids or low-melting solids which were purified by micro-fractionation from traces of potassium hydrogen sulphate or by crystallisation, and showed the expected selective high-intensity absorption in the ultra-violet (see below). On heating or on exposure to light and air, they readily resinify, and some difficulty was experienced in obtaining correct microanalyses, particularly for the tolyl compounds.

The dienes were characterised by their reactions with maleic anhydride and with *p*-benzoquinone in benzene solution, giving respectively the phenyltetrahydrophthalic anhydrides and the phenyl-1 : 4 : 9 : 10-tetrahydronaphtha-5 : 8-quinones (cf. Diels and Alder, *Ber.*, 1929, **62**, 2081, 2337). The tetrahydro-quinones are pale yellow owing to their absorption band near 3650 A. (see below), but slowly change on standing into the colourless phenyl-1 : 4-dihydronaphtha-5 : 8-quinols. This double prototropic change is facilitated by exposure to light, and the ease with which it occurs again appears to parallel that of the isomerisation of the phenylpropenylcarbinols. Thus the *p*-anisyl derivative does not even show the expected light absorption maximum at 3650 A. in hexane, chloroform, or benzene solution; maxima near 3300 A. expected for the 1 : 4-dihydronaphthalene derivative (cf. Morton and de Gouveia, *J.*, 1934, 916) appear instead, and only the colourless quinol can be recovered from the solution. Since the last two solvents are not appreciably transparent to light of wave-lengths shorter than 2350 and 3000 A. respectively at the cell thickness used (1 cm.), the wave-length of the photochemically active light seems to be within the region of the 3650 A. band expected for the tetrahydronaphthaquinone.

The light absorption properties of the various compounds were determined in the region 2150—4000 A. In the phenylpropenylcarbinols (Table I), the phenyl and ethylene chromophores are in isolated positions, and would therefore be expected to contribute independently to the ultra-violet light absorption (cf. Braude, *Ann. Reports*, 1945, **42**, 105). The selective absorption of the ethylenic double bond lies well below 2150 A., and the absorption of the carbinols in the region examined should therefore be closely similar to that of the corresponding substituted toluenes, as is found to be the case.

In the styrylcarbinols (Table II, Figs. 2 and 3), the essential chromophore is the styrene system. Styrene exhibits two bands in the region examined, at 2450 and 2920 A. (Pestemer, Langer, and Manchen, *Monatsh.*, 1936, **68**, 326), which can be assigned to the conjugated system and to the partial phenyl chromophore respectively. The styrylcarbinols exhibit similar bands, showing small bathochromic displacements of 10—180 A. due to the substituents, except that a *p*-fluoro-group produces a hypsochromic shift of 30 A. In the naphthylurethanes

(Table III) the absorption originating in the naphthyl residue is superimposed on the styryl absorption and the difference in the absorption of the naphthylurethanes of the styrylcarbinols and of methanol coincides with the absorption of the styrylcarbinols themselves.

TABLE I.

Ultra-violet light absorption of $C_6H_4R{\cdot}CH(OH){\cdot}CH{:}CHMe$ *in ethanol.**

R.				R.			
H	$\lambda_{max.}$, A.	—	2510, 2580	*p*-F	$\lambda_{max.}$, A.	—	2580, 2640, 2700
	$\epsilon_{max.}$	—	450, 450		$\epsilon_{max.}$	—	1450, 1450, 1050
o-Me	$\lambda_{max.}$, A.	2,150	*2590*, 2640, *2700*, *2810*	*p*-Cl	$\lambda_{max.}$, A.	2,220	2590, 2640
	$\epsilon_{max.}$	11,000	480, 510, 400, 130		$\epsilon_{max.}$	11,000	2300, 2300
m-Me	$\lambda_{max.}$, A.	—	2420, 2515, 2580, 2650, *2700*, *2725*	*p*-Br	$\lambda_{max.}$, A.	2,230	2590, 2650
	$\epsilon_{max.}$	—	1050, 1150, 1450, 1450, 1150, 1000		$\epsilon_{max.}$	13,000	1500, 1500
p-Me	$\lambda_{max.}$, A.	2,220	2595, 2645, 2720	*p*-MeO	$\lambda_{max.}$, A.	2,280	2730, 2760, 2815
	$\epsilon_{max.}$	11,000	270, 310, 280		$\epsilon_{max.}$	13,500	2200, 2200, 2100

Ultra-violet light absorption of $R{\cdot}C_6H_4{\cdot}Me$ *in ethanol for comparison.*

p-Me	$\lambda_{max.}$, A.	2,160	2600, 2680, 2740	*p*-MeO	$\lambda_{max.}$, A.	2,240	2800, 2850
	$\epsilon_{max.}$	7,500	330, 500, 620		$\epsilon_{max.}$	10,400	2200, 1530
p-Br	$\lambda_{max.}$, A.	2,200	2620, 2690, 2770				
	$\epsilon_{max.}$	10,500	390, 470, 390				

* In this and subsequent tables figures in italics refer to inflections.

TABLE II.

Ultra-violet light absorption of $C_6H_4R{\cdot}CH{:}CH{\cdot}CH(OH)Me$ *in ethanol.*

R.			
H	$\lambda_{max.}$, A.	2480, 2510	2810, 2910
	$\epsilon_{max.}$	19,000, 19,500	2000, 1550
o-Me	$\lambda_{max.}$, A.	2480, 2550	2880, 2970
	$\epsilon_{max.}$	16,000, 16,000	1300, 700
m-Me	$\lambda_{max.}$, A.	2510, 2550	*2880*, 2960
	$\epsilon_{max.}$	17,500, 17,500	1300, 900
p-Me	$\lambda_{max.}$, A.	*2460*, 2510, 2550	2890
	$\epsilon_{max.}$	19,000, 22,000, 22,000	1600
p-F	$\lambda_{max.}$, A.	2480, 2580	2800, 2950
	$\epsilon_{max.}$	21,000, 15,000	1500, 800
p-Cl	$\lambda_{max.}$, A.	*2510*, 2560, 2590	2900, 2990
	$\epsilon_{max.}$	22,500, 23,000, 23,000	1700, 1150
p-Br	$\lambda_{max.}$, A.	2580	2880, 2990
	$\epsilon_{max.}$	26,000	2300, 1150
p-MeO	$\lambda_{max.}$, A.	2610, 2690	2920
	$\epsilon_{max.}$	25,000, 19,800	3400

TABLE III.

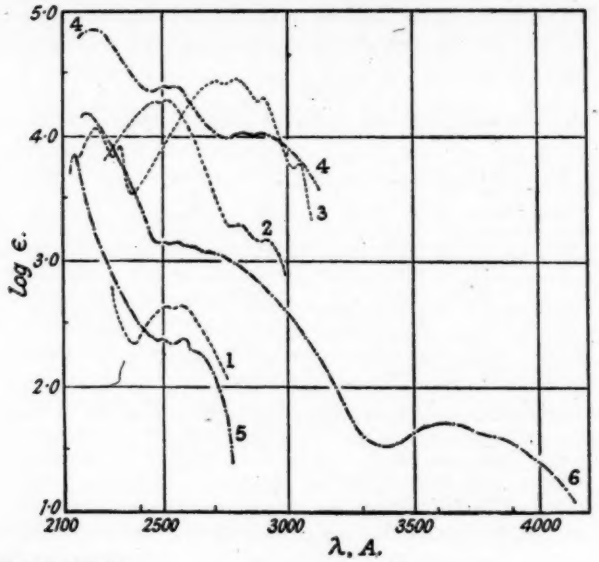
Ultra-violet light absorption of $C_{10}H_7{\cdot}NH{\cdot}CO_2{\cdot}CHMe{\cdot}CH{:}CH{\cdot}C_6H_4R$ *in ethanol.*

R.				
H	$\lambda_{max.}$, A.	2220	2510, 2560	2810, 2900
	$\epsilon_{max.}$	72,000	25,000, 25,000	10,000, 10,000
o-Me	$\lambda_{max.}$, A.	2210	2510	2810, 2910
	$\epsilon_{max.}$	76,000	20,000	9000, 9000
m-Me	$\lambda_{max.}$, A.	2200	2550	2810, 2910
	$\epsilon_{max.}$	75,000	20,000	8600, 8000
p-Me	$\lambda_{max.}$, A.	2210	2550	2800, *2900*, *2960*
	$\epsilon_{max.}$	69,000	20,000	11,000, 9600, 930
p-F	$\lambda_{max.}$, A.	2220	2500	2820, 2910
	$\epsilon_{max.}$	71,000	22,000	7500, 7500
p-Cl	$\lambda_{max.}$, A.	2220	2580	2910
	$\epsilon_{max.}$	68,000	30,000	10,500
p-Br	$\lambda_{max.}$, A.	2220	2580	*2900*
	$\epsilon_{max.}$	71,000	29,000	10,500
p-MeO	$\lambda_{max.}$, A.	2220	2650	2920
	$\epsilon_{max.}$	71,000	35,000	13,000

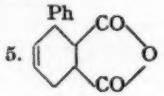
Ultra-violet light absorption of $C_{10}H_7{\cdot}NH{\cdot}CO_2Me$ *in ethanol for comparison.*

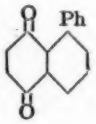
$\lambda_{max.}$, A.	2230	—	2810, 2910
$\epsilon_{max.}$	68,000	—	6800, 6800

FIG. 1.



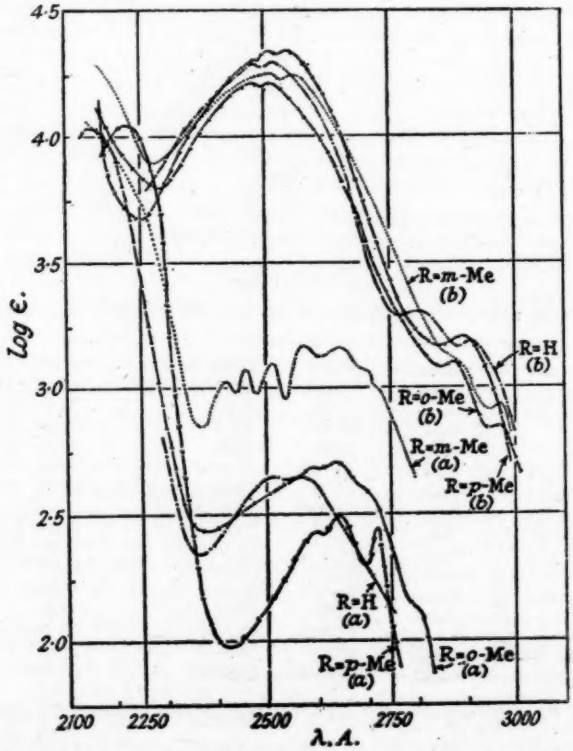
1. Ph·CH(OH)·CH:CHMe.
2. Ph·CH:CH·CH(OH)·Me.
3. Ph·CH:CH·CH:CH_2.
4. Ph·CH:CHMe·O·CO·NH·Naphthyl.

5. 

6. 

(*In ethanol.*)

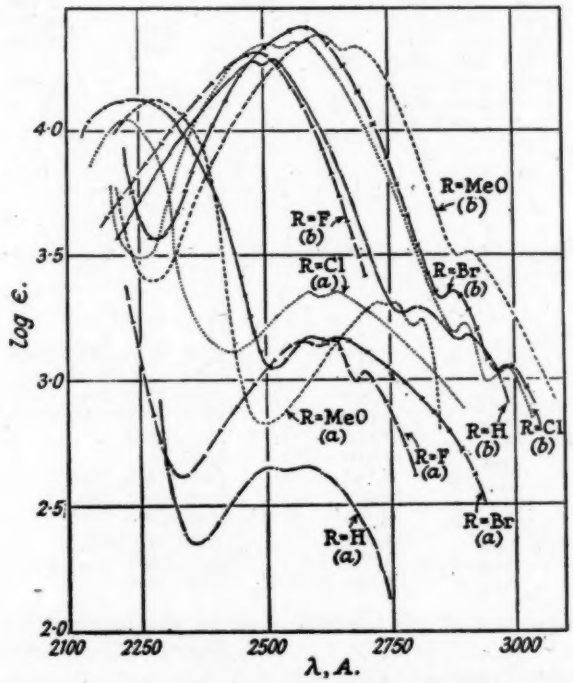
FIG. 2.



(*a*) R·C_6H_4·CH(OH)·CH:CHMe *and* (*b*) R·C_6H_4·CH:CH·CH(OH)Me.
(*In ethanol.*)

The phenylbutadienes (Table IV, Figs. 4 and 5) give rise to resolved absorption bands around 2200, 2800, and 3100 A. The last two may be ascribed respectively to the phenylbutadiene and to the partial phenyl chromophore, while the first probably represents a summation of the low wave-length phenyl bands and absorption due to the partial butadiene chromophore. The effects of methyl, chloro-, and bromo-substituents on the 2800 A. bands is smaller even than in the styryl system, while the fluoro-group again has a hypsochromic effect of 30 A., and the methoxy-group a bathochromic effect of 110 A. In the maleic anhydride

FIG. 3.



(*a*) *p*-R·C_6H_4·CH(OH)·CH:CHMe *and* (*b*) *p*-R·C_6H_4·CH:CH·CH(OH)Me.
(*In ethanol.*)

adducts (Table V), the phenylchromophore is again isolated from the other unsaturated groups in the molecule and the absorption is very similar to that of the phenylpropenylcarbinols. The absorption curves of the benzoquinone adducts (Table VI) are a summation of those due

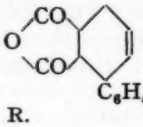
TABLE IV.

Ultra-violet light absorption of C_6H_4R·CH:CH·CH:CH_2 *in ethanol.*

R.				
H	$\lambda_{max.}$, A.	2230, 2330	2710, 2800, 2900	3050
	$\epsilon_{max.}$	12,000, 8500	28,000, 28,300, 27,000	6000
o-Me	$\lambda_{max.}$, A.	2230	2810	*
	$\epsilon_{max.}$	12,500	25,000	
m-Me	$\lambda_{max.}$, A.	2170, 2285, 2350	2790	*3110*
	$\epsilon_{max.}$	16,600, 14,400, 10,000	29,000	7200
p-Me	$\lambda_{max.}$, A.	2270, 2340	*2730*, 2810, 2880	3090
	$\epsilon_{max.}$	11,300, 9250	28,900, 30,000, 28,000	8000
p-F	$\lambda_{max.}$, A.	2180	2730, 2770	*
	$\epsilon_{max.}$	12,800	30,000, 30,000	
p-Cl	$\lambda_{max.}$, A.	2270, 2340	2810, *2860*	*3120*
	$\epsilon_{max.}$	12,200, 7500	32,000, 31,000	5700
p-Br	$\lambda_{max.}$, A.	*2200*, 2270	2810, 2860	*
	$\epsilon_{max.}$	13,600, 12,000	31,000, 30,000	
p-MeO	$\lambda_{max.}$, A.	2220	2840, 2910	*
	$\epsilon_{max.}$	16,000	35,000, 35,000	

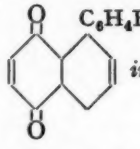
* Absorption beyond 3100 A. not determined.

TABLE V.

Ultra-violet light absorption of  *in ethanol.*

R.				R.			
H	$\lambda_{max.}$, A.	2,150	*2480*, 2580, *2650*	*p*-Cl	$\lambda_{max.}$, A.	2,230	*2470*, 2600, 2670, 2770
	$\epsilon_{max.}$	7,800	260, 270, 190		$\epsilon_{max.}$	12,500	280, 320, 350, 250
o-Me	$\lambda_{max.}$, A.	2,130	2630, 2710	*p*-Br	$\lambda_{max.}$, A.	2,230	2600, 2660, 2770
	$\epsilon_{max.}$	11,500	250, 160		$\epsilon_{max.}$	14,000	350, 350, 200
m-Me	$\lambda_{max.}$, A.	2,145	2650, 2730	*p*-MeO	$\lambda_{max.}$, A.	2,280	2650, 2700, 2720, 2760, 2820
	$\epsilon_{max.}$	11,000	330, 260		$\epsilon_{max.}$	11,500	200, 270, 270, 270, 230
p-Me	$\lambda_{max.}$, A.	2,180	*2600*, 2640, 2730				
	$\epsilon_{max.}$	10,000	320, 350, 320				
p-F	$\lambda_{max.}$, A.	—	2600, 2650, 2710				
	$\epsilon_{max.}$	—	120, 155, 135				

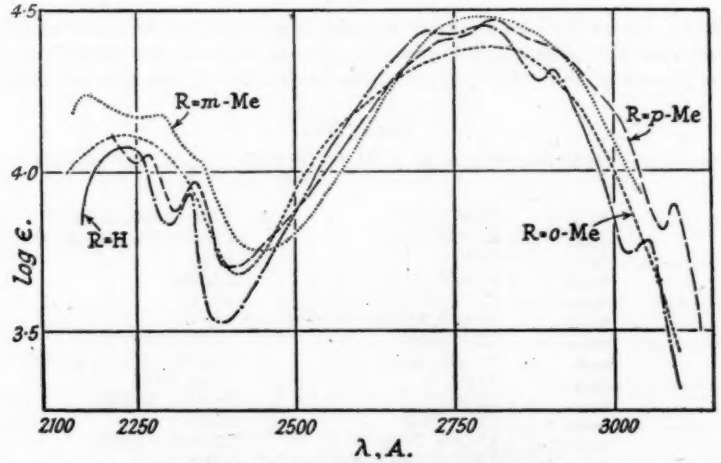
TABLE VI.

Ultra-violet light absorption of  *in n-hexane.*

R.				
H	$\lambda_{max.}$, A.	2,200	2500, 2560, *2610*, *2690*	3640, *3780*
	$\epsilon_{max.}$	15,500	1450, 1400, 1300, 1100	53, 43
o-Me	$\lambda_{max.}$, A.	2,200	2600, 2810, 2910	3650
	$\epsilon_{max.}$	16,500	1400, 1100, 1100	60
p-Me	$\lambda_{max.}$, A.	2,220	2580, *2820*	3640, *3760*
	$\epsilon_{max.}$	19,000	1650, 850	55, 50
p-F	$\lambda_{max.}$, A.	2,180	2550, 2600, 2900	3650
	$\epsilon_{max.}$	23,000	2600, 1800, 850	80
p-Cl	$\lambda_{max.}$, A,	2,250	2550, 2820, 2920	3650
	$\epsilon_{max.}$	24,000	1500, 900, 900	55
p-Br	$\lambda_{max.}$, A.	2,230, 2,270	2490, 2560	3650
	$\epsilon_{max.}$	27,500, 27,000	2400, 2000	55

to their separate phenyl and dihydro-quinone systems, the latter giving rise to bands near 2500 and 3600 A., *i.e.*, displaced by *ca.* 200 A. with respect to those shown by the open-chain diacetyl-ethylene system (Braude, *J.*, 1945, 490) (Fig. 1).

FIG. 4.

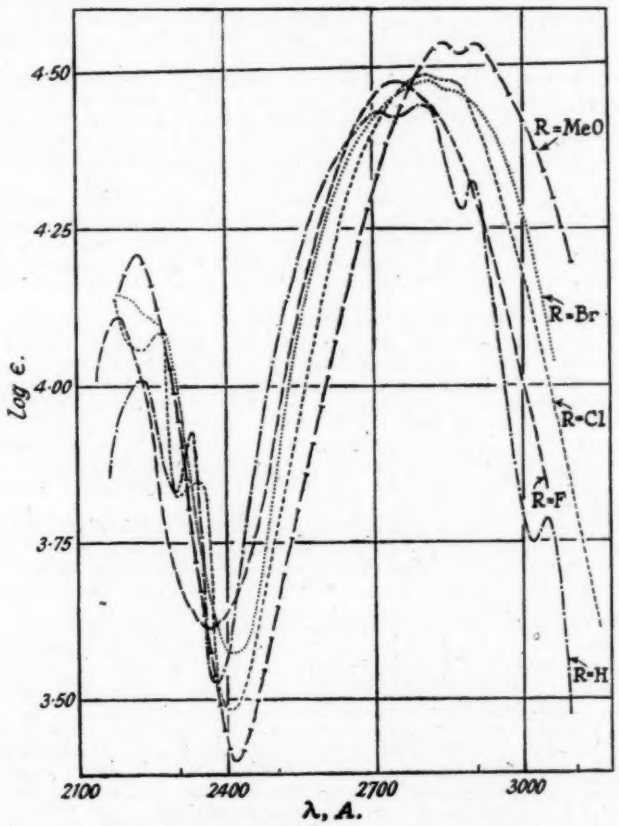


$R{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}CH{:}CH_2$. (*In ethanol.*)

The variochromic effects of the nuclear substituents on the principal bands in the phenylpropenylcarbinols, styrylmethylcarbinols, and phenylbutadienes are summarised in Table VII.

(The exact values of $\Delta\lambda$ are somewhat arbitrary owing to the vibrational structure. The highest peaks have been taken as characteristic of a group, and where two peaks of equal intensity are shown, the one at higher wave-length has been used for computing $\Delta\lambda$.) These effects are generally smallest (10—50 A.) for a methyl substituent, a little larger (10—90 A.) for the halogen groups, and largest (70—180 A.) for the methoxyl group. A number of other regularities appear, but their generality is too limited to warrant separate discussion. The fact, however, that the variochromic effects of nuclear substituents in the styryl and phenylbutadiene systems are no greater than in the phenyl one and smaller than in corresponding

FIG. 5.



p-R·C_6H_4·CH:CH·CH:CH_2. (*In ethanol.*)

TABLE VII.

The variochromic effects of nuclear substituents.

R.	C_6H_4R·CH(OH)·CH:CHMe: "Phenyl" band.	C_6H_4R·CH:CH·CH(OH)Me: "Styrene" band.	"Phenyl" band.	C_6H_4R·CH:CH·CH:CH_2: "Phenylbutadiene" band.	"Phenyl" band.
		$\lambda_{max.}$, A.			
H	2580	2510	2810	2800	3050
		$\Delta\lambda_{max.}$, A.			
o-Me	+ 60	+ 40	+ 70	+ 10	—
m-Me	+ 50	+ 40	+ 70	− 10	+ 60
p-Me	+ 65	+ 40	+ 80	+ 10	+ 40
p-F	+ 60	− 30	− 10	− 30	—
p-Cl	+ 60	+ 80	+ 90	+ 10	+ 70
p-Br	+ 70	+ 70	+ 70	+ 10	—
p-MeO	+ 180	+ 100	+ 110	+ 110	—

systems where the substituents are directly attached to acyclic ethylenic double bonds (cf. Bowden, Braude, and Jones, *J.*, 1946, 948) is of interest. Since the conjugating and transmitting capacity of a group is related to its polarisability (cf. Braude, *loc. cit.*), it provides spectral evidence for the lower polarisability of the phenyl nucleus as compared with an aliphatic ethylenic group.

Experimental.

(Light-absorption data are only given when not included in Tables I—VI.)

o-*Tolylpropenylcarbinol* (I; R = *o*-Me).—Freshly distilled crotonaldehyde (20 g.) in ether (40 c.c.) was added to *o*-tolylmagnesium bromide (from Mg, 6·5 g.) in ether (250 c.c.) during one hour at 0°; the solution was then stirred for 3 hours and treated with excess of ammonium chloride solution. Isolation of the product with ether, drying over anhydrous potassium carbonate, and distillation from a trace of potassium carbonate yielded o-*tolylpropenylcarbinol* (30·5 g.), b. p. 61°/0·001 mm., $n_D^{19°}$ 1·5392 (Found: C, 81·2; H, 8·7. $C_{11}H_{14}O$ requires C, 81·45; H, 8·7%).

o-*Methylstyrylmethylcarbinol* (II; R = *o*-Me).—Treatment of the above carbinol (1·5 g.) with 0·01M-hydrochloric acid in 60% aqueous dioxan (50 c.c.) for 12 hours at 30° yielded o-*methylstyrylmethylcarbinol* (1·35 g.), b. p. 66°/0·005 mm., $n_D^{22°}$ 1·5590 (Found: C, 81·75; H, 8·55. $C_{11}H_{14}O$ requires C, 81·45; H, 8·7%). The *α-naphthylurethane* (0·6 g.), obtained by treating the carbinol (0·33 g.) with α-naphthyl *iso*cyanate (0·35 g.), crystallised from petrol (b. p. 80—100°) in needles, m. p. 104° (Found: C, 79·9; H, 6·5; N, 4·2. $C_{22}H_{21}O_2N$ requires C, 79·75; H, 6·4; N, 4·2%).

1-(o-*Tolyl*)*buta*-1 : 3-*diene*.—*o*-Tolylpropenylcarbinol (4 g.) was distilled from potassium hydrogen sulphate (0·8 g.) at 10^{-3} mm. The *diene* after fractionation had b. p. 37°/0·01 mm., $n_D^{17°}$ 1·6008 (Found: C, 91·0; H, 8·5. $C_{11}H_{12}$ requires C, 91·6; H, 8·4%). The maleic anhydride *adduct* (0·65 g.) was obtained by refluxing the diene (0·5 g.) with maleic anhydride (0·25 g.) in benzene (3 c.c.) for 5 minutes. It crystallised from petrol (b. p. 80—100°) in fine needles, m. p. 92° (Found: C, 73·9; H, 5·8. $C_{15}H_{14}O_3$ requires C, 74·35; H, 5·3%).

p-*Benzoquinone adduct*. A solution of the diene (5·0 g.) and *p*-benzoquinone (3·5 g.) in benzene (15 c.c.) was boiled for a few minutes. On cooling, and evaporation of the solvent under reduced pressure, crystals separated which were washed with a little methanol to remove a small amount of quinhydrone. Recrystallisation from petrol (b. p. 80—100°) afforded pale yellow plates of 1-(o-*tolyl*)-1 : 4 : 9 : 10-*tetrahydronaphthaquinone* (3·7 g.), m. p. 93·5° (Found: C, 80·9; H, 6·25. $C_{17}H_{16}O_2$ requires C, 80·95; H, 6·4%). On allowing the quinone (1 g.) to stand overnight with acetic anhydride (25 g.) and zinc chloride (0·5 g.) and dilution with water, 1-(o-*tolyl*)-1 : 4-*dihydronaphthaquinol diacetate* (1 g.) was obtained; it crystallised from petrol (b. p. 80—100°) or alcohol, and had m. p. 141° (Found: C, 74·9; H, 6·1. $C_{21}H_{20}O_4$ requires C, 74·9; H, 6·0%). Light absorption in alcohol: Maxima at 2180, 2650, and 2720 A., ϵ = 25,000, 800, and 720, respectively.

m-*Tolylpropenylcarbinol* (I; R = *m*-Me).—Freshly distilled crotonaldehyde (9·5 g.) in ether (50 c.c.) was added to *m*-tolylmagnesium bromide (from Mg, 3·2 g.) during one hour at 0°, and the solution stirred for 3 hours. Working up in the usual manner and distillation from a trace of potassium carbonate yielded m-*tolylpropenylcarbinol* (17 g.), b. p. 76°/0·01 mm., $n_D^{19°}$ 1·5384 (Found: C, 81·8; H, 8·7. $C_{11}H_{14}O$ requires: C, 81·45; H, 8·7%).

m-*Methylstyrylmethylcarbinol* (II; R = *m*-Me).—Treatment of the above carbinol (1·5 g.) with 0·01M-hydrochloric acid in 60% dioxan (50 c.c.) for 24 hours at 30° yielded m-*methylstyrylmethylcarbinol* (1·30 g.), b. p. 69°/0·005 mm., $n_D^{18°}$ 1·5608 (Found: C, 81·7; H, 8·65. $C_{11}H_{14}O$ requires C, 81·45; H, 8·7%). The *α-naphthylurethane* crystallised from petrol (b. p. 80—100°); m. p. 96° (Found: C, 79·8; H, 6·6; N, 4·2. $C_{22}H_{21}O_2N$ requires C, 79·75; H, 6·4; N, 4·25%).

1-(m-*Tolyl*)*buta*-1 : 3-*diene*.—*m*-Tolylpropenylcarbinol (2·5 g.) was distilled from potassium hydrogen sulphate (0·25 g.) at 10^{-3} mm. Fractionation of the product from potassium hydrogen sulphate (0·1 g.) yielded the *diene* (1·8 g.), b. p. 80°/0·005 mm., $n_D^{17°}$ 1·5980 (Found: C, 89·5; H, 8·5. $C_{11}H_{12}$ requires C, 91·6; H, 8·4%). The maleic anhydride *adduct* was obtained by treating the diene (0·5 g.) with maleic anhydride (0·3 g.) in benzene (3 c.c.). Crystallisation from light petroleum (b. p. 60—80°) yielded the adduct (0·7 g.) in long needles, m. p. 78° (Found: C, 74·35; H, 5·8. $C_{15}H_{14}O_3$ requires C, 74·35; H, 5·8%).

p-*Tolylpropenylcarbinol* (I; R = *p*-Me).—Freshly distilled crotonaldehyde (35 g.) in ether (70 c.c.) was added to *p*-tolylmagnesium bromide (from Mg, 12 g.) in ether (300 c.c.) during one hour at 0°, and the solution stirred for 3 hours. Isolation of the product in the usual manner afforded p-*tolylpropenylcarbinol* (65 g.), which crystallised from light petroleum (b. p. 40—60°) in needles, m. p. 55° (Found: C, 81·55; H, 8·65. $C_{11}H_{14}O$ requires C, 81·45; H, 8·7%).

p-*Methylstyrylmethylcarbinol* (II; R = *p*-Me).—Treatment of the above carbinol (1 g.) with 0·001M-hydrochloric acid in 60% aqueous dioxan (50 c.c.) for 15 hours at 30° yielded p-*methylstyrylmethylcarbinol* (0·86 g.), which crystallised from light petroleum (b. p. 40—60°) in needles, m. p. 43° (Found: C, 81·3; H, 8·55. $C_{11}H_{14}O$ requires C, 81·45; H, 8·7%). The *α-naphthylurethane* crystallised from petrol (b. p. 80—100°) in needles, m. p. 135°, or from methanol, m. p. 127° (Found: C, 79·45; H, 6·4; N, 4·05. $C_{22}H_{21}O_2N$ requires C, 79·75; H, 6·4; N, 4·25%).

1-(p-*Tolyl*)*buta*-1 : 3-*diene*.—*p*-Tolylpropenylcarbinol (2 g.) was distilled from potassium hydrogen sulphate (0·2 g.) at 10^{-2} mm. The diene, b. p. 78°/0·005 mm., solidified at room temperature and after crystallisation from aqueous methanol had m. p. 26° (Found: C, 90·6; H, 8·55. $C_{11}H_{12}$ requires C, 91·6; H, 8·4%). The maleic anhydride *adduct* was obtained by treating the diene (1·5 g.) with maleic anhydride (1 g.) in benzene (10 c.c.). Crystallisation from petrol (b. p. 80—100°) yielded the adduct (2·3 g.) in long needles, m. p. 117° (Found: C, 74·6; H, 5·8. $C_{15}H_{14}O_3$ requires C, 74·35; H, 5·8%).

p-*Benzoquinone adduct*. Treatment of the diene (2·2 g.) with *p*-benzoquinone (1·8 g.) in benzene (10 c.c.) afforded p-*tolyl*-1 : 4 : 9 : 10-*tetrahydronaphtha*-5 : 8-*quinone* (2·8 g.), which crystallised from

petrol (b. p. 80—100°) in pale yellow plates, m. p. 114° (Found : C, 81·4; H, 6·3. $C_{17}H_{16}O_2$ requires C, 81·0; H, 6·4%).

p-*Fluorophenylpropenylcarbinol* (I, R = *p*-F).—*p*-Bromofluorobenzene (58 g.) (Schieman and Pilarsky, *Ber.*, 1931, **64**, 1343) in ether (250 c.c.) was added slowly to a suspension of magnesium (8·0 g.) in ether (150 c.c.) containing ethyl bromide (0·5 g.) and stirred for 4 hours in an atmosphere of nitrogen. Freshly distilled crotonaldehyde (23 g.) in ether (50 c.c.) was added to the ice-cold suspension during 2 hours, and stirring continued overnight. On working up in the usual manner, p-*fluorophenylpropenylcarbinol* (37 g.) was obtained, b. p. 59°/0·001 mm., $n_D^{15°}$ 1·5175 (Found : C, 72·2; H, 7·0. $C_{10}H_{11}OF$ requires C, 72·25; H, 6·7%). Active hydrogen (Zerewitinoff) : 1·02.

p-*Fluorostyrylmethylcarbinol* (II; R = *p*-F).—Treatment of the above carbinol (1·5 g.) with 0·01M-hydrochloric acid in 60% aqueous dioxan (50 c.c.) for 36 hours at 30° yielded p-*fluorostyrylmethylcarbinol* (1·4 g.), b. p. 78°/0·01 mm., $n_D^{20°}$ 1·5411, which solidified on standing at room temperature and after crystallisation from light petroleum (b. p. 40—60°) had m. p. 42° (Found : C, 72·3; H, 6·95. $C_{10}H_{11}OF$ requires C, 72·25; H, 6·7%). The *α-naphthylurethane* crystallised from petrol (b. p. 80—100°) in needles, m. p. 116° (Found: C, 75·5; H, 5·7; N, 4·1. $C_{21}H_{18}O_2NF$ requires C, 75·2; H, 5·4; N, 4·2%).

l-(p-*Fluorophenyl*)*buta*-1 : 3-*diene*.—*p*-Fluorophenylpropenylcarbinol (2·5 g.) was distilled from potassium hydrogen sulphate (0·25 g.) at 10^{-2} mm. The product was fractionated from potassium hydrogen sulphate (0·1 g.) and p-*fluorophenylbutadiene* (1·7 g.) was obtained, b. p. 37°/0·001 mm., $n_D^{22°}$ 1·5788, which solidified on cooling and had m. p. 16—16·5° (Found : C, 80·4; H, 6·6. $C_{10}H_9F$ requires C, 80·65; H, 6·5%). The maleic anhydride *adduct* (0·25 g.) was obtained by treating the diene (0·18 g.) with maleic anhydride (0·12 g.) in benzene (5 c.c.). Crystallisation from petrol (b. p. 80—100°) yielded the adduct in needles, m. p. 113° (Found : C, 68·5; H, 4·7. $C_{14}H_{11}O_3F$ requires C, 68·3; H, 4·5%).

p-*Benzoquinone adduct*. The diene (1·2 g.) was treated with *p*-benzoquinone (0·67 g.) in benzene (5 c.c.). Crystallisation from petrol (b. p. 80—100°) afforded l-p-*fluorophenyl*-1 : 4 : 9 : 10-*tetrahydronaphtha*-5 : 8-*quinone* (0·93 g.) as very pale yellow needles, m. p. 90° (Found : C, 74·8; H, 5·3. $C_{16}H_{13}O_3F$ requires C, 75·0 H, 5·1%).

p-*Chlorophenylpropenylcarbinol* (I; R = *p*-Cl).—*p*-Dichlorobenzene (74 g.) in ether (400 c.c) was slowly added to a suspension of magnesium (12 g.) in ether (100 c.c.) containing ethyl bromide (0·5 g.) and refluxed for 96 hours. Freshly distilled crotonaldehyde (35 g.) in ether (70 c.c.) was added during one hour at 0°, and the solution was stirred for 3 hours. Working up in the usual manner yielded unchanged *p*-dichlorobenzene (23 g.) and p-*chlorophenylpropenylcarbinol* (28 g.), b. p. 89°/0·005 mm., $n_D^{21°}$ 1·5471 (Found : C, 65·9; H, 6·2; Cl, 19·3. $C_{10}H_{11}OCl$ requires C, 65·7; H, 6·05; Cl, 19·4%). Active hydrogen (Zerewitinoff) : 1·02.

p-*Chlorostyrylmethylcarbinol* (II; R = *p*-Cl).—Treatment of the above carbinol (1 g.) with 0·01M-hydrochloric acid in 60% aqueous dioxan (50 c.c.) for 40 hours at 30° yielded p-*chlorostyrylmethylcarbinol* (0·87 g.), which separated from light petroleum (b. p. 40—60°) in needles, m. p. 63° (Found : C, 65·95; H, 6·0. $C_{10}H_{11}OCl$ requires C, 65·75; H, 6·1%). *α-Naphthylurethane*. (i) A mixture of *p*-chlorostylrylmethylcarbinol (0·5 g.) and α-naphthyl *iso*cyanate (0·5 g.) was kept in a sealed tube for 5 days. The *urethane* crystallised from petrol (b. p. 80—100°) in needles, m. p. 128° (Found : C, 71·5; H, 5·35. $C_{21}H_{18}O_2NCl$ requires C, 71·6; H, 5·6%). (ii) *p*-Chlorophenylpropenylcarbinol (0·5 g.) was treated with α-naphthyl *iso*cyanate (0·5 g.). The oily product after one crystallisation from aqueous ethanol had m. p. 69°. On successive crystallisations from ethanol and finally petrol, the m. p. rose to 128° [undepressed by the product obtained under (i)], and the light absorption maximum, not originally present, at 2580 A., $\epsilon = 30{,}000$ (see Table III), appeared.

l-(p-*Chlorophenyl*)*buta*-1 : 3-*diene*.—*p*-Chlorophenylpropenylcarbinol (2 g.) was distilled from potassium hydrogen sulphate (0·5 g.) at 10^{-2} mm., and the product fractionated. The *diene* (1·55 g.), b. p. 49°/0·002 mm., $n_D^{20°}$ 1·6202, solidified on cooling and had m. p. 18·5° (Found : Cl, 21·75. $C_{10}H_9Cl$ requires Cl, 21·55%). The maleic anhydride *adduct*, obtained by the routine method and crystallised from petrol (b. p. 80—100°), had m. p. 108° (Found : Cl, 13·3. $C_{14}H_{11}O_3Cl$ requires Cl, 13·5%).

p-*Benzoquinone adduct*. Treatment of the diene (1·6 g.) with *p*-benzoquinone (1·2 g.) yielded the pale yellow adduct, l-p-*chlorophenyl*-1 : 4 : 9 : 10-*tetrahydronaphtha*-5 : 8-*quinone* (1·8 g.); after being washed with methanol and crystallised from petrol (b. p. 80—100°) it had m. p. 110° (Found : C, 70·35; H, 4·8; Cl, 12·85. $C_{16}H_{13}O_3Cl$ requires C, 70·45; H, 4·8; Cl, 13·0%).

p-*Bromophenylpropenylcarbinol* (I; R = *p*-Br).—*p*-Dibromobenzene (60 g.) in ether (150 c.c.) was slowly added to a suspension of magnesium (6 g.) in ether (100 c.c.) containing ethyl bromide (0·5 g.) and refluxed for 24 hours. Freshly distilled crotonaldehyde (17 g.) in ether (50 c.c.) was added during one hour at 0° and the solution was stirred for 3 hours. Working up in the usual manner yielded unchanged *p*-dibromobenzene (5 g.) and p-*bromophenylpropenylcarbinol* (26 g.), b. p. 92°/0·002 mm., $n_D^{22°}$ 1·5739, which solidified on cooling and after crystallisation from light petroleum (b. p. 40—60°) had m. p. 27° (Found : C, 52·7; H, 5·15; Br, 36·0. $C_{10}H_{11}OBr$ requires C, 52·9; H, 4·9; Br, 35·2%).

p-*Bromostyrylmethylcarbinol* (II; R = *p*-Br).—Treatment of the above carbinol (1·5 g.) with 0·1M hydrochloric acid in 60% aqueous dioxan (50 c.c.) for 12 hours yielded p-*bromostyrylmethylcarbinol* (1·4 g.) as needles, from light petroleum (b. p. 40—60°), m. p. 66° (Found : C, 53·2; H, 5·0. $C_{10}H_{11}OBr$ requires C, 52·9; H, 4·9%). The *α-naphthylurethane* (0·55 g.) crystallised from petrol (b. p. 80—100°) in needles, m. p. 139° (Found : C, 64·0; H, 4·55; N, 3·85. $C_{21}H_{18}O_2NBr$ requires C, 63·65; H, 4·55; N, 3·55%).

l-(p-*Bromophenyl*)*buta*-1 : 3-*diene*.—*p*-Bromophenylpropenylcarbinol (2 g.) was distilled from potassium hydrogen sulphate (0·5 g.) at 10^{-2} mm. The product was fractionated, giving the *diene* (1·5 g.), b. p. 88°/0·001 mm., which solidified at room temperature, and crystallised from aqueous methanol; m. p. 29° (Found : C, 57·05; H, 4·7. $C_{10}H_9Br$ requires C, 57·45; H, 4·35%). The maleic anhydride *adduct*, obtained as usual and crystallised from petrol (b. p. 80—100°), formed fine needles, m. p. 138·5° (Found : C, 55·0; H, 3·65. $C_{14}H_{11}O_3Br$ requires C, 54·75; H, 3·6%).

p-*Benzoquinone adduct*. Treatment of the diene (0·5 g.) with *p*-benzoquinone (0·25 g.) in benzene (5 c.c.) gave the adduct, l-p-*bromophenyl*-1 : 4 : 9 : 10-*tetrahydronaphtha*-5 : 8-*quinone* (0·45 g.), which

crystallised from petrol (b. p. 80—100°) in pale yellow rectangular plates, m. p. 105° (Found: C, 60·4; H, 3·95. $C_{14}H_{13}O_3Br$ requires C, 60·6; H, 4·15%).

p-*Anisylpropenylcarbinol* (I; R = *p*-MeO).—*p*-Bromoanisole (35 g.) in ether (100 c.c.) was added slowly to a suspension of magnesium (4·45 g.) in ether (250 c.c.) containing ethyl bromide (0·5 g.) and stirred overnight in an atmosphere of nitrogen. Freshly distilled crotonaldehyde (12 g.) in ether (25 c.c.) was added during one hour at 0° and the solution was stirred for 3 hours. Working up in the usual manner and final distillation from a trace of potassium carbonate yielded p-*anisylpropenylcarbinol* (23·5 g.), b. p. 100°/0·005 mm., $n_D^{17°}$ 1·5454, which partly solidified on standing at 0°; m. p. 13—15° (Found: C, 74·45; H, 8·0. $C_{11}H_{14}O_2$ requires C, 74·15; H, 7·9%). Active hydrogen (Zerewitinoff): 1·01.

p-*Methoxystyrylmethylcarbinol* (II; R = *p*-MeO).—Treatment of the above carbinol (1 g.) with 0·001M-hydrochloric acid in 60% aqueous dioxan (50 c.c.) for 3 hours at 30° yielded p-*methoxystyrylmethylcarbinol* (0·95 g.), in needles from light petroleum (b. p. 40—60°); m. p. 79° (Found: C, 73·95; H, 7·9. $C_{11}H_{14}O_2$ requires C, 74·15; H, 7·9%). Active hydrogen (Zerewitinoff): 1·02. The *α-naphthylurethane* (0·4 g., 0·8 g. respectively) was obtained by warming (i) *p*-anisylpropenylcarbinol (0·5 g.) and (ii) *p*-methoxystyrylmethylcarbinol (0·5 g.) with α-naphthyl *iso*cyanate (0·5 g.), and crystallised from petrol (b. p. 80—100°) in needles, m. p. 101° (Found: N, 4·1. $C_{22}H_{21}O_3N$ requires N, 4·05%).

1-(p-*Anisyl*)*buta*-1 : 3-*diene*.—*p*-Anisylpropenylcarbinol (1 g.) was warmed with potassium hydrogen sulphate at 10^{-2} mm. for about 5 minutes, and then rapidly distilled. p-*Anisylbutadiene* (0·7 g.) solidified on standing and was crystallised from aqueous methanol, m. p. 46° (Found: C, 82·2; H, 7·45. $C_{11}H_{12}O$ requires C, 82·45; H, 7·55%). Knorr (D.R.-P. 544388; *Chem. Abs.*, 1932, **26**, 2467) gives b. p. 124°/6 mm. for the diene obtained by dehydration of *p*-anisylallylcarbinol. The maleic anhydride *adduct* crystallised from petrol (b. p. 80—100°) in fine needles, m. p. 145° (Found: C, 70·0; H, 5·4. $C_{15}H_{14}O_4$ requires C, 69·75; H, 5·45%).

p-*Benzoquinone adduct*. Treatment of the diene (0·53 g.) with *p*-benzoquinone (0·33 g.) in benzene (5 c.c.) yielded 1-p-*anisyl*-1 : 4 : 9 : 10-*tetrahydronaphthaquinone* (0·38 g.), pale yellow plates from petrol (b. p. 80—100°); m. p. 103° (Found: C, 76·35; H, 6·0. $C_{17}H_{16}O_3$ requires C, 76·05; H, 6·0%). Light absorption in *n*-hexane: Maxima at 2280, 2680, and 3250 A., ϵ = 23,300, 2500, and 230, respectively. The absorption may be ascribed to the isomer, 1-*p*-anisyl-1 : 4-dihydronaphtha-5 : 9-quinol (needles, m. p. 168°), which is produced on irradiation with ultra-violet light during the absorption measurements and separates from the solution on standing or evaporation.

1-*Phenylbuta*-1 : 3-*diene*.—Freshly distilled cinnamaldehyde (40 g.) in ether (120 c.c.) was added to methylmagnesium iodide (from Mg, 8 g.) in ether (200 c.c.). Decomposition of the complex with excess of ammonium chloride solution, isolation with ether, distillation from a trace of potassium hydrogen sulphate, and finally fractionation afforded pure phenylbutadiene, b. p. 45°/0·5 mm., $n_D^{17°}$ 1·6125, which solidified on cooling and had m. p. 4° (Klages, *Ber.*, 1904, **37**, 2309, gives b. p. 86°/11 mm.; Muskat and Herrman, *J. Amer. Chem. Soc.*, 1931, **53**, 252, give b. p. 86°/11 mm., $n^{28°}$ 1·5950; Emerson, *J. Org. Chem.*, 1945, **10**, 464, gives b. p. 89—94°/14 mm., $n_D^{25°}$ 1·6010). The low refractive indices recorded by these authors are probably due to the presence of considerable proportions of undehydrated styrylmethylcarbinol or of polymers of the diene (cf. Stobbe and Reiss, *Ber.*, 1912, **45**, 3496; Wright, *J. Org. Chem.*, 1936, **1**, 457). Light absorption: see Table IV (Stobbe and Reiss, *loc. cit.*, and Smakula, *Angew. Chem.*, 1934, **47**, 657, give maximum at 2800 A., ϵ = 24,000). The maleic anhydride adduct, crystallised from petrol (b. p. 80—100°), had m. p. 120° (Diels and Alder, *Ber.*, 1929, **62**, 2081, give m. p. 120°).

p-*Benzoquinone adduct*. Phenylbutadiene (2 g.) was treated with *p*-benzoquinone (2 g.) in benzene (20 c.c.), and the solution boiled for some minutes. On cooling and evaporation of the solvent under reduced pressure, crystals separated, which were washed with methanol to remove a small amount of quinhydrone. *Phenyl*-1 : 4 : 9 : 10-*tetrahydronaphtha*-5 : 8-*quinone* (2·25 g.) crystallised from petrol (b. p. 80—100°) in pale yellow rectangular plates, m. p. 101° (Found: C, 80·7; H, 5·9. $C_{16}H_{14}O_2$ requires C, 80·65; H, 5·9%).

Styrylmethylcarbinol α-naphthylurethane. Prepared from styrylmethylcarbinol (Braude, Jones, and Stern, *J.*, 1946, 396) (0·5 g.) and α-naphthyl *iso*cyanate (0·5 g.), the *urethane* crystallised from petrol (b. p. 80—100°) in needles, m. p. 89·5° (Found: C, 79·25; H, 6·1; N, 4·2. $C_{21}H_{19}O_2N$ requires C, 79·45; H, 6·05; N, 4·4%).

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206. *The Kinetics of Anionotropic Rearrangement. Part VI. The Effects of Methyl, Methoxy-, and Halogen Substituents attached to a Phenyl Group.*

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The kinetics of the acid-catalysed oxotropy of substituted phenylpropenylcarbinols to the corresponding styrylmethylcarbinols (p. 1097, I ⟶ II) have been studied. The effects of nuclear substituents in this molecular rearrangement are in accord with those observed in substitution reactions and in the dissociation constants of substituted benzoic acids. The reaction is facilitated by methyl and methoxyl substituents, and retarded by halogen substituents, first-order rate constants at one temperature varying in the order *p*-Br < *p*-Cl < *p*-F < H < *m*-Me < *o*-Me < *p*-Me < *p*-MeO. The differences in the rate constants are due to small

changes both in the isodielectric energy of activation and in the non-exponential factor of the Arrhenius equation. The results are discussed in terms of the electronic effects of the substituent groups and the unexpected sequence previously noted by other authors of tautomeric effects decreasing in the order F > Cl > Br, is confirmed.

In previous papers in this series, detailed investigations have been described of rearrangements of the type where X is an acetylenic, ethylenic, or phenyl group. A reaction mechanism has

$$X{\cdot}C(OH){\cdot}C{=}C \longrightarrow X{\cdot}C{=}C{\cdot}C{\cdot}OH$$

been outlined which accounts for the kinetic features of the reaction and their dependence on medium composition The effects of many aliphatic substituents have been examined and found to be those expected for a reaction requiring electron accession at the point of reaction. It appeared worth while to extend this work to a study of the effects of aromatic substituents, data for which have hitherto been largely derived from substitution reactions and dissociation constants.

It was shown in Part V (*J.*, 1946, 396) that the rearrangement of phenylpropenylcarbinol (I, R = H) to styrylmethylcarbinol (II, R = H) proceeds smoothly in aqueous dioxan in the presence of hydrochloric acid, that the reaction follows the first-order law, and that the rate constants are practically independent of the carbinol concentration, roughly proportional to the acid concentration (c_A) when $c_A \ll 0{\cdot}1$M, and decreased by increasing dioxan concentration (c_S) when $c_S \ll 80\%$ v/v. The same characteristics apply to the rearrangements of substituted

$$\text{(I.)}\quad C_6H_4R{\cdot}CH(OH){\cdot}CH{:}CHMe \longrightarrow C_6H_4R{\cdot}CH{:}CH{\cdot}CH(OH)Me \quad \text{(II.)}$$

phenylpropenylcarbinols (I) where R = *o*-Me, *m*-Me, *p*-Me, *p*-F, *p*-Cl, *p*-Br, and *p*-MeO (Tables I, II, and III). The rate constants determined at 10° intervals between 30° and 60° accurately obey the Arrhenius equation.

It was previously observed (Part V, *loc. cit.*) that in the rearrangements of phenylvinyl- and phenylpropenyl-carbinols, the highest extinction coefficients reached in kinetic runs were lower by some 3—8% than those of the pure styryl isomers isolated from the reaction mixture, and it was suggested that the formation of stereoisomers or the establishment of equilibria at 92—97% rearrangement was among the more likely explanations of the discrepancies. With

TABLE I.

The effect of carbinol concentration.

First-order rate constants (10^4k, min.$^{-1}$) for the rearrangement of $C_6H_4R{\cdot}CH(OH){\cdot}CH{:}CHMe$ in 60% (by vol.) aqueous dioxan at 30·0°. c_{ROH} = carbinol concentration (% w/v); c_A = hydrochloric acid concentration (mols./l.).

R =	H.	*p*-Me.	*p*-Cl.	*p*-MeO.
c_{ROH}.	$c_A = 0{\cdot}01$M.	$c_A = 0{\cdot}001$M.	$c_A = 0{\cdot}01$M.	$c_A = 0{\cdot}0001$M.
0·020	185	154	40·0	179
0·10	184	161	40·8	185
0·500	180	157	36·2	177

TABLE II.

The effect of acid concentration.

First-order rate constants for the rearrangement of $C_6H_4R{\cdot}CH(OH){\cdot}CH{:}CHMe$ in 60% (by vol.) aqueous dioxan at 30·0°. c_A = hydrochloric acid concentration (mols./l.).

c_A.	10^4k (min.$^{-1}$).	k/c_A.	c_A.	10^4k (min.$^{-1}$).	k/c_A.
	R = H.			R = *p*-F.	
0·002	34·7	1·74	0·002	29·9	1·50
0·01	184	1·84	0·01	146	1·46
0·1	1760	1·76	0·1	1520	1·52
	R = *p*-Me.			R = *p*-Cl.	
0·0001	15·0	15·0	0·001	4·34	0·434
0·001	161	16·1	0·01	40·8	0·410
0·01	1540	15·4	0·1	432	0·432
	R = *p*-MeO.			R = *p*-Br.	
0·0001	185	185	0·001	3·40	0·340
0·001	1890	189	0·01	35·2	0·352
0·002	3660	183	0·1	365	0·365

TABLE III.

Temperature and solvent effects.

First-order rate constants (10^4k, min.$^{-1}$) for the rearrangement of $C_6H_4R{\cdot}CH(OH){\cdot}CH{:}CH{\cdot}CH_3$. Carbinol concentration 0·1% (w/v) throughout. c_A = Hydrochloric acid concentration (mols./l.). c_B = Dioxan concentration (% v/v).

		R = H.	*o*-Me.	*m*-Me.	*p*-Me.	*p*-F.	*p*-Cl.	*p*-Br.	*p*-MeO.
t.	c_B.	c_A = 0·01	0·001	0·001	0·001	0·01	0·01	0·01	0·0001
0·0°	40	25·5	5·17	2·96	22·9	19·2	4·60	3·59	177
	60	5·40	1·18	0·56	3·98	3·62	0·83	0·75	31·5
30·0	40	716	139	80·9	406	580	135	127	647
	60	184	35·9	21·7	161	146	40·8	35·2	185
40·0	40	1,890	382	163	1,300	1550	436	364	1340
	60	545	127	62·7	414	401	99·8	94·5	521
50·0	40	4,500	840	408	3,060	3900	1070	865	2960
	60	1,510	281	195	1,080	1200	302	272	1290
60·0	40	11,700	2350	1380	10,200	9390	2770	2350	5930
	60	3,650	910	571	2,900	2902	908	778	2780

the substituted phenylpropenylcarbinols, the ratios of "kinetic" to "preparative" end-values vary from 0·87 to 0·97, and are again temperature-independent within the experimental error ($\gtrsim \pm 2\%$) (see Experimental). Now, since the type and number of bonds broken and formed in the reaction is otherwise equal and opposite, the heat of reaction should be of the same order as the additional resonance energy of the conjugated (styryl) system, *i.e. ca.* 5 kg.-cals./mol. (Pauling and Sherman, *J. Chem. Physics*, 1933, **1**, 606; Kistiakowsky, Ruhoff, Smith, and Vaughan, *J. Amer. Chem. Soc.*, 1936, **58**, 146). This corresponds to an approximately two-fold change in the equilibrium constant for a temperature change from 30° to 60°, and to a change in conversion from 95 to 90%, *i.e.*, only just more than the limit of experimental error. The present data are thus indecisive. If equilibrium formation does take place, the over-all rate constants k actually represent the sum $(k_1 + k_{-1})$ of the rate constants of the forward and backward reactions $ROH \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} R'OH$, but the values of k_1 will only be 3—13% lower than those of k, and the values of the Arrhenius parameters will hardly be affected.

It was pointed out in Part II (*J.*, 1944, 443) that two types of solvent effect may be distinguished in considering the dependence of the rate constants, energies of activation, etc., of a catalysed reaction on the reaction medium. Those directly affecting the reactants were termed primary solvent effects, while those resulting in the first place in a change in the catalytic properties, such as the proton-donating properties, of the medium were termed secondary solvent effects. Evidence was adduced for both types of effects in oxotropic rearrangements.

It was shown that in the rearrangement of propenylethynylcarbinol in aqueous ethanol the decrease in rate constant with increasing concentration of organic solvent (c_B) could be expressed in the form $\log k = mD + n$ where D is the dielectric constant, and m and n are constants and $c_B \ll 80\%$. This was interpreted mainly as a secondary solvent effect, the decrease in dielectric constant resulting in a decrease in the proton-donating properties of the medium. It was further shown that on this basis a correction could be applied to the Arrhenius energy of activation to allow for the change in dielectric constant of the medium with temperature, the *isodielectric energy of activation* being given by $E_{[D]} = E_{Arr.} + RT_1T_2mb$ where T_1, T_2 are the limits of the temperature range investigated, and b is a constant defined by $D = a + bt$, t being the temperature in °C. Whereas $E_{Arr.}$ varied considerably with solvent composition, $E_{[D]}$ was independent of it within the limits of experimental error. Similar observations were made (Part V, *loc. cit.*) with the rearrangement of phenylpropenylcarbinol in aqueous ethanol and aqueous dioxan, though $E_{[D]}$ in the latter case was *ca.* 4 kg.-cals./mol. lower than in the former, the difference being ascribed to a primary solvent effect, namely, increased solvation of the carbinol group by the dioxan.

The independence of $E_{[D]}$ of medium composition thus applies only as long as there is no appreciable change in solvating properties. Independent evidence for the occurrence of primary solvent effects was provided by the small but definite variations in the slope of the $\log k$–c_A, and $\log k$–c_s plots with different substituted ethylenic and acetylenic carbinols (Parts III and IV, *J.*, 1946, 122, 128). These variations are presumably due to small differences in the extent of solvation of the carbinols by the solvent. If secondary solvent effects alone came into play, these slopes should be the same for different compounds undergoing the same reaction by

identical mechanisms. The data now obtained for substituted phenylpropenylcarbinols also indicate the occurrence of both primary and secondary solvent effects.

Specific * and relative rate constants, dielectric constant effects (expressed as m, the slope of the rate constant–dielectric constant plot), Arrhenius and isodielectric energies of activation, and reaction constants A (defined by $k/c_A = Ae^{-E_{[D]}/RT}$) † are given in Table IV; m varies somewhat for different carbinols, being lower when R = Me or MeO, and higher when R = Halogen, as compared with R = H (see I). But whereas values of $E_{Arr.}$ for any one carbinol are higher by 2—3 kg.-cals./mol. for 60% as compared with 40% aqueous dioxan, the corresponding values of $E_{[D]}$ differ by not more than 0·4 kg.-cal./mol. in seven cases, and by 0·9 kg.-cal./mol. when R = *p*-MeO. Within the range examined, the energy of activation is thus again independent, or nearly so, of the composition and hence of the dielectric constant of the medium, when allowance is made for the different temperature coefficients of the dielectric constants of different media.

TABLE IV.

Specific and relative rate constants, Arrhenius parameters, and isodielectric energies of activation for the rearrangement of $C_6H_4R{\cdot}CH(OH){\cdot}CH{:}CHMe$ in aqueous dioxan (percentage of dioxan given in parentheses). r = Rate constant relative to phenylpropenylcarbinol (R = H).

R.	k/c_A for 0·001M-HCl, (60%), 30·0°.	m.	$E_{Arr.}$ (40%).	$E_{Arr.}$ (60%).	$E_{[D]}$ (40%).	$E_{[D]}$ (60%).	log A (60%).	r.	10^5K.*
H	1·79	0·033	18·2	19·5	20·7	20·6	13·3	1	6·3
o-Me	3·59	0·032	18·2	19·5	20·7	20·6	13·6	2·0	12·3
m-Me	2·17	0·028	18·8	20·4	21·0	21·4	14·0	1·2	5·4
p-Me	16·1	0·033	18·1	19·6	20·7	20·7	14·4	9·0	4·2
p-F	1·50	0·036	17·7	19·4	20·5	20·7	13·4	0·84	7·2
p-Cl	0·434	0·036	19·6	20·3	22·2	21·6	13·4	0·24	10·6
p-Br	0·340	0·034	19·3	20·4	21·9	21·6	13·3	0·19	10·7
p-MeO	189	0·029	15·7	17·9	18·0	18·9	14·1	105	3·4

* Dissociation constants of $C_6H_4R{\cdot}CO_2H$ in water at 25° (Dippy, *Chem. Reviews*, 1939, **25**, 206).

Regarding the correlation of rate constants, energies of activation, and reaction constants with substituents, this may be summarised as follows: (i) The rate constants are increased by methyl substituents in the order H < *m*-Me < *o*-Me < *p*-Me, strongly increased by a *p*-MeO group, and decreased by *p*-halogen substituents in the order H > *p*-F > *p*-Cl > *p*-Br. (ii) Isodielectric energies of activation are constant at 20·6 (±0·1) kg.-cals./mol. when R = H, *o*-Me, *p*-Me or *p*-F, slightly increased (by 0·3—1·5 kg.-cals./mol.) when R = *m*-Me, *p*-Cl or *p*-Br and decreased (by 2 kg.-cals./mol.) when R = *p*-MeO. (iii) Reaction constants (A) are constant at 13·4 (±0·1) sec.$^{-1}$ when R = H or Halogen, and slightly increased by R = Me in the order *o*-Me < *m*-Me < *p*-Me, and by R = MeO.

In aqueous-ethanolic media, the first-order law is obeyed when R = H, *p*-Me, *p*-F, or *p*-MeO, but with the *p*-Cl and *p*-Br substituted carbinols the first-order rate constants fall as the reaction proceeds (see Experimental) in a manner reminiscent of that previously observed with phenylvinylcarbinol (Part V, *loc. cit.*) and shown there to be due to etherification occurring before, as well as simultaneously with, rearrangement.

EXPERIMENTAL.

Materials.—The preparation and properties of the phenylpropenylcarbinols and of their styryl isomers are described in the preceding paper. Dioxan was purified by the method of Hesse and Frahm (*Ber.*, 1938, **71**, 2629).

Kinetic Measurements.—The technique was the same as described in Part V (*loc. cit.*) and preceding papers. Initial and end values are given as $E^{1\%}_{1cm.}$ [= log $(I_0/I)/cl$, where I_0 = intensity of incident light, I = intensity of transmitted light, c = concentration in % w/v, l = cell length in cm.] (Table V).

Typical runs for each carbinol, in aqueous dioxan and ethanol media, are reproduced below. The first-order rate constants (k) are calculated by $k = (2{\cdot}3/z)\log[(a - x_0)/(a - x)]$, where z = time in

* Since k is not directly proportional to c_A when $c_A > 0{\cdot}1$M in the present reaction, the specific rate constants (k/c_A) are *not* equal to k when $c_A = 1$M. Nevertheless for purposes of comparison of different series, specific rate constants are obviously preferable to k's at an arbitrary acid concentration. The values given in Parts III and IV (J., 1946, 122, 128, Tables III, cols. 1) for the rearrangement of acetylenyl- and vinyl-carbinols should be divided by 10^3 to convert them into k/c_A. Although these measurements refer to 60% aqueous ethanol media, the specific constants are then comparable to the present ones, since rate constants in 60% dioxan and ethanol are not appreciably different (see below and Part V, *loc. cit.*).

† In a catalysed reaction, A depends on the catalyst concentration, and the choice of the latter is arbitrary. For purposes of standardisation it appears preferable to base A on the specific rate constant k/c_A. The values given in Parts III and IV (*locc. cit.*, cols. 3) should accordingly be increased by 1·0.

TABLE V.

R.	$\lambda_{max.}$, A.	Initial $E^{1\%}_{1\,cm.}$	Final $E^{1\%}_{1\,cm.}$, "kinetic."	Final $E^{1\%}_{1\,cm.}$, "preparative."	Ratio (col. 4/col. 5).
H	2510	20	1260	1300	0·97
o-Me	2550	35	900	990	0·91
m-Me	2550	250	1030	1080	0·95
p-Me	2550	20	1300	1340	0·97
p-F	2480	90	1170	1260	0·93
p-Cl	2560	130	1100	1270	0·87
p-Br	2580	60	990	1120	0·87
p-MeO	2610	120	1300	1400	0·93

minutes, x_0 = absorption intensity at $t = 0$, x = absorption intensity at t mins., and a = final absorption intensity, intensities being expressed as $E^{1\%}_{1\,cm.}$ at the wave-length of the maximum chosen. In the rearrangement of *p*-chloro- and *p*-bromo-phenylpropenylcarbinol in 80% aqueous ethanol, the rate constants clearly fall as the reaction proceeds, and are extrapolated to zero time. In all other runs, the maximum deviation allowed in individual k's was ±5%. The maximum error in averaged k's should not exceed ±2%.

Rearrangements of $C_6H_4R{\cdot}CH(OH){\cdot}CH{:}CHMe$ *in* 60% *(by vol.) aqueous dioxan, hydrochloric acid at* 30·0°. [c_{ROH} = carbinol concentration (% w/v), c_A = acid concentration (mol./l.).]

(i) R = *o*-Me. $c_{ROH} = 0{\cdot}1$, $c_A = 0{\cdot}001$.

Time (mins.)	0	60	105	159	1440	
$E^{1\%}_{1\,cm.}$ (2550 A.)	35	205	305	410	900	
10^4k (min.$^{-1}$)	—	36·5	35·6	35·7	—	(Mean) 35·9

(ii) R = *m*-Me. $c_{ROH} = 0{\cdot}1$, $c_A = 0{\cdot}001$.

Time (mins.)	0	90	150	210	1440	
$E^{1\%}_{1\,cm.}$ (2550 A.)	250	390	470	530	1030	
10^4k (min.$^{-1}$)	—	22·0	22·0	21·1	—	(Mean) 21·7

(iii) R = *p*-Me. $c_{ROH} = 0{\cdot}1$, $c_A = 0{\cdot}001$.

Time (mins.)	0	30	50	70	90	600	
$E^{1\%}_{1\,cm.}$ (2550 A.)	20	500	740	880	1000	1300	
10^4k (min.$^{-1}$)	—	157	165	159	162	—	(Mean) 161

(iv) R = *p*-F. $c_{ROH} = 0{\cdot}1$, $c_A = 0{\cdot}01$.

Time (mins.)	0	20	40	60	79	600	
$E^{1\%}_{1\,cm.}$ (2480 A.)	90	370	570	710	830	1170	
10^4k (min.$^{-1}$)	—	150	147	142	145	—	(Mean) 146

(v) R = *p*-Cl. $c_{ROH} = 0{\cdot}1$, $c_A = 0{\cdot}01$.

Time (mins.)	0	60	120	180	240	1440	
$E^{1\%}_{1\,cm.}$ (2560 A.)	130	340	500	630	750	1100	
10^4k (min.$^{-1}$)	—	40·6	40·8	40·3	41·4	—	(Mean) 40·8

(vi) R = *p*-Br. $c_{ROH} = 0{\cdot}1$, $c_A = 0{\cdot}01$.

Time (mins.)	0	58	98	142	201	1440	
$E^{1\%}_{1\,cm.}$ (2580 A.)	60	190	275	360	470	990	
10^4k (min.$^{-1}$)	—	27·7	27·9	28·1	29·4	—	(Mean) 28·3

(vii) R = *p*-MeO. $c_{ROH} = 0{\cdot}1$, $c_A = 0{\cdot}001$.

Time (mins.)	0	2	3·5	5	6·5	30	
$E^{1\%}_{1\,cm.}$ (2610 A.)	120	480	680	860	960	1300	
10^4k (min.$^{-1}$)	—	1820	1840	1970	1910	—	(Mean) 1890

Rearrangements of $C_6H_4R{\cdot}CH(OH){\cdot}CH{:}CHMe$ *in* 80% *(by vol.) aqueous ethanol, hydrochloric acid at* 50·0°, *except* (v). [c_{ROH} and c_A as above.]

(i) R = *p*-Me. $c_{ROH} = 0{\cdot}1$, $c_A = 0{\cdot}002$.

Time (mins.)	0	4	8	12	16	360	
$E^{1\%}_{1\,cm.}$ (2550 A.)	20	450	720	920	1040	1300	
10^4k (min.$^{-1}$)	—	1030	990	1010	1000	—	(Mean) 1000

(ii) R = *p*-F. $c_{ROH} = 0{\cdot}2$, $c_A = 0{\cdot}02$.

Time (mins.)	0	1	2	3	4	5	120	
$E^{1\%}_{1\,cm.}$ (2480 A.)	90	195	290	390	470	525	1200	
10^4k (min.$^{-1}$)	—	1020	1020	1080	1080	1030	—	(Mean) 1050

(iii) R = *p*-Cl. $c_{ROH} = 0{\cdot}1$, $c_A = 0{\cdot}02$.

Time (mins.)	0	6	12	15	18	21	24	27	600
$E^{1\%}_{1\,cm.}$ (2560 A.)	130	340	470	530	570	600	625	655	1100
10^4k (min.$^{-1}$)	*450* *	406	359	354	335	308	297	288	—

(iv) R = *p*-Br. $c_{ROH} = 0{\cdot}2$, $c_A = 0{\cdot}02$.

Time (mins.)	0	5	10	15	20	25	30	1440
$E^{1\%}_{1\,cm.}$ (2580 A.)	80	220	350	450	525	590	630	990
10^4k (min.$^{-1}$)	*420* *	400	385	357	376	340	320	—

(v) R = *p*-MeO. $c_{ROH} = 0{\cdot}2$, $c_A = 0{\cdot}001$, $t = 30{\cdot}0°$.

Time (mins.)	0	2	3	4	5	6	7	8	120	
$E^{1\%}_{1\,cm.}$ (2610 A.) ...	120	360	475	550	630	700	780	840	1300	
10^4k (min.$^{-1}$)	—	1140	1180	1130	1120	1130	1170	1180	—	(Mean) 1150

* Extrapolated.

Discussion.

With regard to the reaction mechanism, this is clearly the same throughout the series, since such characteristics as reaction order, dependence of the rate constants on carbinol, acid, and solvent concentrations, and the independence of the isodielectric energies of activation of solvent composition are the same in each case. The interpretation of substituent effects can therefore be based on the mechanism already outlined and discussed for the rearrangement of the parent compound, phenylpropenylcarbinol (Part V, *loc. cit.*).*

Table IV shows that the differences in the rate constants are due to variations in both the energy of activation and the non-exponential factor A of the Arrhenius equation. Except with the *p*-methoxy-compound, however, where $E_{[D]}$ is distinctly lower, while A is only slightly higher than for phenylpropenylcarbinol, these variations are only small and mostly entail differences of the same order of magnitude as the experimental error. In view of this fact, only tentative conclusions can be based on such regularities as can be discerned, and it will be preferable at this stage of the investigation to limit the discussion mainly to a consideration of the changes in the relative rate constants brought about by substituents.

Ingold's classification (*J.*, 1933, 1120; *Chem. Reviews*, 1934, **15**, 233; see also Baker, "Tautomerism," Routledge, London, 1934; Remick, "Electronic Interpretation of Organic Chemistry," Wiley, New York, 1943) of substituent effects, which is now generally accepted, recognises two principal types: (i) the general inductive (I) and (ii) the tautomeric effect (T). The former depends on the capacity of the atom or group to attract or repel electrons and is mainly electrostatic in origin, I being negative with respect to hydrogen (electron-attraction) when the electronegativity of the substituent is greater than that of hydrogen, *i.e.*, when $\chi_R > \chi_H$, and positive (electron-repulsion) when $\chi_R < \chi_H$. The tautomeric effect, on the other hand, depends on the capacity of a substituent to share an additional electron pair, *i.e.*, on its capacity for covalency increase or decrease, and on its capacity to favour resonance forms of the type $R^+{=}A{-}B^-$ or $R^-{=}A{-}B^+$ in systems classically represented by R—A=B. In the case of alkyl groups, the central atom carries no unshared electron-pair and their tautomeric effect must be ascribed to no-bond resonance in the C—H links, *i.e.*, contributions from $H^+C{=}C{-}C^-$ to systems classically represented by H—C—C=C (Baker, *J.*, 1939, 1150).

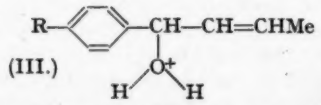
In the mechanism proposed for the present reaction, both steps require electron accession at the point of reaction and k should therefore be increased by $+I$ and $+T$ effects and retarded by $-I$ effects. This has been shown to be the case for alkyl and alkenyl substituents attached to the aliphatic part of the molecule (Parts III, IV, and V, *locc. cit.*). Similarly, the present data for the three tolylpropenylcarbinols are in accordance with expectations, the accelerating effect of the methyl substituent being least in the *m*-position ($+I$ effect only) and larger in the *o*- and *p*-positions ($+I$ and $+T$ effects). The fact that the increase in k due to an *o*-methyl group is less than that of a *p*-methyl group, although the $+I$ and probably the $+T$ effect should be greater for the former, provides yet another example of the well-known "ortho"-effect: the decrease in planarity due to the ortho-substituent inhibits the transmission of the T effect. However, even the "true" $+T$ effect is unlikely to be much larger in the *ortho*-

* The kinetic criterion given in Part V (*loc. cit.*, p. 403, lines 42 and 43) is erroneous. A valid criterion for the distinction between $ROH + H^+ \xrightarrow{slow} ROH_2^+ \xrightarrow{fast} R'OH_2^+$, and $ROH + H^+ \xrightarrow{fast} ROH_2^+ \xrightarrow{slow} R'OH_2^+$ was correctly stated in Part II (*J.*, 1944, 443) and depends on the linear relation between $\log k$ and the acidity function H_0, rather than between $\log k$ and c_A.

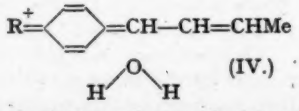
than in the *para*-position, and the roughly tenfold increase in k due to a methyl substituent in the phenyl ring may be compared with its much larger effect when attached to the ethylenic double bond. Thus phenylpropenylcarbinol rearranges about 500 times faster than phenylvinylcarbinol under identical conditions (Part V, *loc. cit.*). This large difference is to be ascribed to the fact that the double-bond electron-pair moves towards the (electron-repelling) methyl substituent in one case, and away from it in the other, as well as possibly to a greater polarisability (allowing a readier transmission of the $+T$ effect) of the ethylenic double bond as compared with the aromatic system.

A *p*-MeO group also has the expected accelerating influence owing to its large $+T$ effect, but with the halogeno-carbinols the results are not entirely those to be anticipated from *a priori* considerations. The $-I$ effect should lead to reduction in the rate constant and to the sequence F< Cl <Br <H, since the electronegativity differences are in this order (F 4·0, Cl 3·0, Br 2·8, H 2·1; Pauling, " Nature of the Chemical Bond," Cornell, 1940). The $+T$ effect should counteract this diminution, but since it should be largest for Br and least for F and since it is smaller than the $-I$ effect, the actual sequence F <Cl <Br< H should remain unaltered. The observed sequence is the reverse, *i.e.*, Br< Cl< F< H, which means that the $+T$ effects vary in the order F> Cl> Br and not F <Cl < Br. This is unexpected, since the control of the nucleus over the valency electrons should decrease, and the capacity for covalency increase on ascending a group of the periodic table. Similar results indicating a reversed sequence of the tautomeric effects in the halogens have been observed in several other cases (Shoppee, *J.*, 1933, 696; Baddeley, Bennett, *et al.*, *J.*, 1933, 261, 1112; 1935, 1827). It must be emphasised, however, that this interpretation is based on the tacit assumption that the rate constants as such, rather than the energies of activation and reaction constants separately, represent an adequate and additive measure of I and T effects.

It is noteworthy that the *p*-methoxyl substituent, which is the only one producing a large (*i.e.*, over 100-fold) change in rate, results in pronounced lowering of the energy of activation ($\Delta E_{[D]} = ca.$ 2 kg.-cals.), just as the 500-fold increase in rate due to the β-methyl group in phenylpropenyl- as compared with phenylvinyl-carbinol is accompanied by a large decrease in $E_{[D]}$ of *ca.* 5 kg.-cals./mol. (Part V, *loc. cit.*). The data for the rearrangements of acetylenyl- and vinyl-carbinols (Parts III and IV, *locc. cit.*) also bear out that, on the whole, an increase in rate is accompanied by a decrease in the energy of activation,* and that large changes in rate depend on large changes in the energy of activation rather than log A. This is readily interpreted as indicating that although the effect of substituents is exerted to a small extent by changes in the equilibrium constant of the preceding proton-transfer equilibrium, $ROH + H^+ \rightleftharpoons ROH_2^+$, their main effect lies in altering the energy requirements of the rate-determining isomerisation $ROH_2^+ \longrightarrow R'OH_2^+$. An electron-repelling substituent increases the electron-density at the point of reaction, through increased contribution from resonance forms such as (IV), thereby partly neutralises the positive charge at the reaction centre, and decreases the energy of separation of the carbonium ion and the dipolar water molecule. The existence of extended conjugation in the resonance form of the oxonium ions of phenylpropenylcarbinols may also explain why substituents exerting $+T$ effects enhance the tendency for equilibrium formation : rearrangement to the styryl isomer results in increased conjugation, and hence, lowering in potential energy, only in the " ordinary " form (III), but not in the resonance form (IV).



(III.)



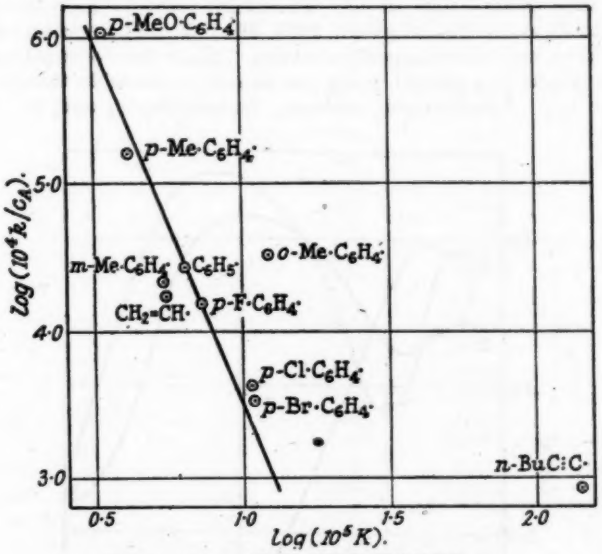
(IV.)

From a qualitative study of the rearrangement–acetylation of *p*-methylstyrylphenyl- and *p*-chlorostyrylphenyl-carbinols, and of *p*-tolyl- and *p*-chlorophenyl-vinylcarbinols, Burton and Ingold (*J.*, 1928, 904) and Burton (*J.*, 1928, 1650) concluded that the reaction is facilitated in the order *p*-Cl·C_6H_4> *p*-Me·C_6H_4> Ph, and that this was the expected order of reactivity. However, since the mechanism postulated by these authors, though different from the one adopted here, also requires electron-accession at the point of reaction, and since the overall electron-attracting effect of the halogens ($-I > +T$) is well known from aromatic substitution and other reactivity

* This conclusion was not drawn in the two papers referred to and only holds if the uncertain values of E (marked ~) for a few of the carbinols are disregarded. It now appears probable that the possibility, already envisaged in Part III, of equilibria being set up in these cases does apply, and that the E values derived from the temperature coefficients of the over-all rate constants do not represent real energies of activation in these cases.

data, this expectation is clearly incorrect, and the expected sequence should be Me·C_6H_4 > Ph > Cl·C_6H_4 as confirmed by the present data. Moreover, inspection of the experimental results of Burton and Ingold also appears to indicate this sequence of reactivity and not the one deduced by their authors. Thus phenylvinyl- and *m*- and *p*-tolylvinyl-carbinols are stated to be converted completely into the corresponding styrylcarbinyl acetates by treatment with boiling acetic anhydride for six hours, while identical treatment of *p*-chlorophenylcarbinol is stated to lead to a mixture containing only *ca.* 70% of the rearranged acetate. It may well be that the probable equilibrium formation in the rearrangements of *p*-chloro- and *p*-bromo-phenylpropenylcarbinols (see above) is enhanced in the less reactive phenylvinyl homologues.

The electron-attracting effect of the chloro- and bromo-substituents is also well illustrated by the fact that they appear to facilitate ether formation in ethanolic acid solution sufficiently for it to occur before rearrangement; with a fluoro-substituent the effect is not sufficiently great to lead to a falling first-order constant. Unlike the rearrangement reaction, which depends on the fission of the carbon–oxygen bond and electron accession at the point of reaction,



k = *Rate constant of* R·CH(OH)·CH:CHMe.
K = *Dissociation constant of* R·CO_2H (*see Table IV*).

ether formation probably depends on the bimolecular fission of the hydrogen–oxygen bond, *i.e.*, on electron recession at the point of reaction.

Rearrangement: $ROH + H^+ \rightleftharpoons ROH_2^+ \longrightarrow [R\cdots OH_2]^+ \longrightarrow R'OH_2^+$

Etherification: $ROH + EtOH_2^+ \longrightarrow \begin{matrix} RO\cdots H \\ Et\cdots OH_2^+ \end{matrix} \longrightarrow \begin{matrix} ROEt \\ + \\ H_3O^+ \end{matrix}$

The ease of etherification of phenylvinylcarbinol (Part V, *loc. cit.*) is similarly to be ascribed to the strong electron-attraction ($-I$ effect) of the free vinyl group; in phenylpropenylcarbinol this is counteracted by the electron-repelling ($+I$, $+T$) effects of the β-methyl group and no etherification occurs prior to rearrangement.

Some correlation might again be expected between the specific rate constants of the carbinols and the dissociation constants (K) of the corresponding benzoic acids (cf. Parts IV and V, *locc. cit.*). The plot of log k/c_A against log K does in fact approximate to a straight line (Table IV; Fig.), except when R = *o*-Me. This is another instance of the "ortho"-effect (cf. Hammett, "Physical Organic Chemistry," McGraw Hill, New York, 1941). The point for vinylpropenylcarbinol (Part IV, *loc. cit.*) also falls on the straight line, but the points for ethynylpropenyl- and hexynylpropenyl-carbinols do not, and thus both the acetylenic groups and not the ethynyl group only, as previously thought, behave differently in this respect from the other groups so far examined.

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207. *Studies in Light Absorption. Part IV. Nitro-olefins.*

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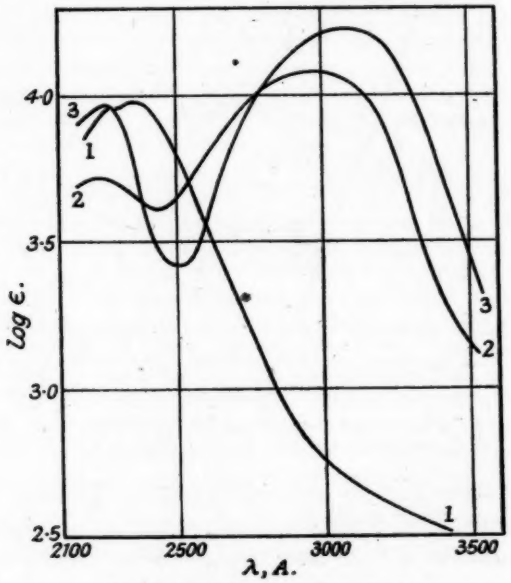
The ultra-violet light absorption of a number of compounds containing the conjugated chromophoric systems C:C·X, C:C·C:C·X, and Ph·C:C·X where X = NO_2 has been examined, and found to be similar to that of the corresponding systems where X = C:C, C:N, C:O, etc.

IT is well known that chromophoric systems of the type C:C·X, where X is a covalently unsaturated group such as C:C, C:N, or C:O, all exhibit selective high-intensity absorption in the 2200 A. region (cf. Braude, *Ann. Reports*, 1945, **42**, 105). The spectral properties of nitro-olefins (X = NO_2) have not hitherto been recorded. Since the conjugating properties of the nitro-group when attached to a phenyl group are known to resemble those of other covalently unsaturated groups (*e.g.*, nitrobenzene, styrene, benzaldehyde, and its *N*-methylimide all



Light absorption (in ethanol) of:

1. CHMe:CH·NO_2. 2. CHMe:CH·CH:CH·NO_2. 3. Ph·CH:CH·NO_2.

exhibit similar ultra-violet light absorption due to the chromophoric system Ph·X), the nitro-olefin system C:C·N$\langle^{O}_{O}$ would also be expected to absorb intensely in the 2200 A. region. Data for a number of representative compounds (Table; Fig.) show that this expectation is fulfilled, but the maxima are situated at somewhat longer wave-lengths than in the formally related C:C·C:O and C:C·C$\langle^{O}_{OH}$ systems.

Although an isolated nitro-group, just as a carbonyl group, gives rise to a low-intensity band near 2700 A. (Zelinsky and Rosanoff, *Z. physikal. Chem.*, 1912, **78**, 629; Goodeve, *Trans. Faraday Soc.*, 1934, **30**, 504; Kortüm, *Z. physikal. Chem.*, 1939, *B*, **43**, 271), nitro-olefins exhibit no band corresponding to the displaced carbonyl band at 3200 A. shown by αβ-ethylenic carbonyl compounds. The solvent effects in the two systems are similar, $\lambda_{max.}$ (ethanol) being higher than $\lambda_{max.}$ (*n*-hexane) by an average of *ca.* 100 A. with the nitro-olefins,

and by *ca.* 70 A. with αβ-ethylenic carbonyl compounds (Woodward, *J. Amer. Chem. Soc.*, 1941, **63**, 1123; 1942, **64**, 72; Evans and Gillam, *J.*, 1945, 432). On the other hand, in the case of the nitro-olefins, vibrational structure appears to be more pronounced in ethanol than in hexane, which is unexpected since the former is generally the more highly solvating solvent.

Lengthening of the conjugated chain as in the α-nitrobutadiene and β-nitrostyrene systems, *i.e.*, C:C·C:C·NO_2 and Ph·C:C·NO_2, respectively, results in the expected increase in $\lambda_{max.}$ and the positions of the long wave-length bands are again 200—300 A. higher than those of the corresponding bands shown by the C:C·C:C·C:O and Ph·C:C·C:O systems. The persistence of shorter wave-length bands, probably to be ascribed to the partial chromophore C:C·NO_2, is peculiar to the nitro-compounds.

The effects of auxochromic substituents are similar to those observed in other systems (cf. Part III, *J.*, 1946, 948); $\lambda_{max.}$ is increased by alkyl and halogen substituents attached to the αβ-ethylenic bond, thus, $\Delta\lambda_{Me}$ = *ca.* 100 A., and $\Delta\lambda_{Br}$ = *ca.* 300 A. in the nitro-ethylenes. In the nitrostyrene system the effects are smaller or negative, thus, for β-substituents $\Delta\lambda_{Me} = -50$ A., $\Delta\lambda_{Cl} = 100$ A., and $\Delta\lambda_{Br} = 150$ A.

Ultra-violet light absorption of nitro-olefins in ethanol and n-*hexane.*

	Ethanol.		*n*-Hexane.	
	$\lambda_{max.}$, A.	$\epsilon_{max.}$	$\lambda_{max.}$, A.	$\epsilon_{max.}$
CH_2:CMe·NO_2	2250	3,300	*	*
CHMe:CH·NO_2	2290	9,400	2290	8,700
	2350	9,700		
CHMe:CMe·NO_2	2340	5,600	2350	6,100
	2420	5,800		
	2500	5,600		
CMe_2:CH·NO_2	2450	8,600	2350	10,000
	2510	8,600		
CHPrβ:CMe·NO_2	2420	6,000	2340	5,400
	2510	6,200	2420	5,600
	2580	6,000		
CHMe:CBr·NO_2	2250	4,000	*	*
	2690	4,800		
CHMe:CH·CH:CH·NO_2	2260	5,500	*	*
	2980	12,000		
CHPh:CH·NO_2	2270	9,500	2230	10,300
	3090	16,500	2290	9,700
			2990	17,800
CHPh:CMe·NO_2	2260	10,300	2230	9,500
	3050	12,400	2930	11,400
CHPh:C~Cl·NO_2	2260	10,600	*	*
	3200	13,600		
CHPh:CBr·NO_2	2260	8,700	*	*
	3240	12,000		

* Not determined.

Experimental.

For the technique of the light absorption measurements, see Part I (*J.*, 1945, 490). The compounds examined had the following physical constants: 2-Nitroprop-1-ene, b. p. 68—70°/144 mm., $n_D^{22°}$ 1·4309; 1-nitroprop-1-ene, b. p. 45°/1·5 mm., $n_D^{19°}$ 1·4663 (Schmidt and Rutz, *Ber.*, 1928, **61**, 2142); 2-nitro-but-2-ene, b. p. 47—50°/9 mm., $n_D^{19°}$ 1·4616; 1-nitro-2-methylprop-1-ene, b. p. 48—49°/9·5 mm., $n_D^{17°}$ 1·4723 (Haitinger, *Annalen*, 1878, **193**, 368; *Monatsh.*, 1881, **2**, 286); 2-nitro-4-methylpent-2-ene, b. p. 67°/10 mm., $n_D^{19°}$ 1·4579; 1-bromo-1-nitroprop-1-ene, b. p. 59—60°/11 mm., $n_D^{17°}$ 1·5121; 1-nitropenta-1 : 3-diene, b. p. 78—79°/2·5 mm., $n_D^{22°}$ 1·5543; β-nitrostyrene, m. p. 57—58° (Worall, *Org. Synth.*, Coll. Vol. I, p. 413); β-nitro-β-methylstyrene, m. p. 64°; β-chloro-β-nitrostyrene, m. p. 48° (Priebs, *Annalen*, 1884, **225**, 321); β-bromo-β-nitrostyrene, m. p. 66° (Worall, *J. Amer. Chem. Soc.*, 1921, **43**, 919). They were prepared either according to the methods given in the references cited, or by methods which will be described in a separate publication. We are indebted to Drs. R. L. Heath and H. A. Piggott of I.C.I. Ltd., Dyestuffs Division, for a sample of 2-nitro-4-methylpent-2-ene.

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208. *Syntheses in the Thiopyran Series. Part I. Tetrahydro-derivatives.*

By Ralph F. Naylor.

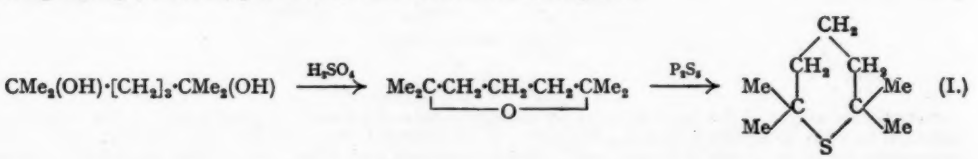
Reaction of a 1 : 5-dibromo-compound with sodium sulphide is not applicable to the synthesis of those members of the tetrahydrothiopyran series which contain tertiary carbon atoms in the 2- and the 6-position. In such cases it is possible to achieve the synthesis by cyclisation of the appropriate 2 : 6-diol to give the corresponding tetrahydropyran, followed by reaction of the latter with phosphorus pentasulphide. By this method 2 : 2 : 6 : 6-tetramethyl- and 2 : 2 : 6-trimethyl-6-ethyl-tetrahydrothiopyran have been prepared.

Recorded investigation of compounds of the tetrahydrothiopyran series has been limited to two of the simplest members, pentamethylene sulphide and 1-methylpentamethylene sulphide, which have been readily obtained by reaction of the appropriate dihalide with sodium sulphide (Clarke, *J.*, 1912, **101**, 1805; v. Braun, *Chem. Zentr.*, 1909, II, 1994; Grischkewitsch-Trochimowski, *Chem. Zentr.*, 1923, I, 1503). A few of the corresponding saturated thiopyrones have been prepared either by addition of hydrogen sulphide to a keto-diene or by cyclisation of a suitable aliphatic sulphide (Arndt and co-workers, *Ber.*, 1925, **58**, 1633; 1930, **63**, 313, 2393; Bennett and Scorah, *J.*, 1927, 194), but otherwise no work has been recorded on this class of compound.

Although pentamethylene bromide reacts fairly readily with sodium sulphide, the yields of tetrahydrothiopyran are less than those reported to be obtainable with the chloride. This is in accord with the work of Bost and Conn (*Oil and Gas J.*, 1933, **32**, No. 3, 17), who obtained only 30% of 2-methyltetrahydrothiopyran from 1 : 5-dibromohexane. In the present work it was desired to prepare tetra-substituted 2 : 6-derivatives, and to this end 2 : 6-dibromo-2 : 6-dimethylheptane was synthesised from ethyl glutarate:

$$CO_2Et\cdot[CH_2]_3\cdot CO_2Et \xrightarrow{MeMgI} CMe_2(OH)\cdot[CH_2]_3\cdot CMe_2\cdot OH \xrightarrow{HBr} CMe_2Br\cdot[CH_2]_3\cdot CMe_2Br$$

On trial, however, the lability of the bromine attached to the tertiary carbon atoms proved to be such that reaction of the bromide with sodium sulphide in alcoholic solution resulted only in the replacement of Br by OEt, and the corresponding reaction without a solvent resulted in loss of hydrogen bromide with formation of monobromodimethylheptenes and geraniolene (C_9H_{16}). This failure necessitated recourse to the less attractive method presented by conversion of a suitable pyran into the sulphur analogue. 2 : 6-Dimethylheptane-2 : 6-diol had already been observed to cyclise when it was heated in the presence of mineral acid, so giving 2 : 2 : 6 : 6-tetramethyltetrahydropyran * (Bruylants, *Rec. Trav. chim.*, 1910, **29**, 130). This pyran was found to give a small yield of the desired 2 : 2 : 6 : 6-*tetramethyltetrahydrothiopyran* (I) when it was heated with phosphorus pentasulphide. The reaction, however, was complex, giving accompanying (resinous) products, which were not investigated.



(I.)

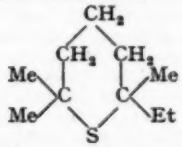
Synthesis of unsymmetrical members of the thiopyran series presented greater difficulty, but since the essential oxide–sulphide conversion must remain the same in view of the presence of tertiary groupings, the only concern was the building up of the required carbon

* It is to be noted that no isomerisation involving shift of the ·OH groups, such as has been observed by Franke and Gomolka (*Monatsh.*, 1929, **56**, 331) in the case of $\alpha\omega$-diols, $CH_2(OH)\cdot[CH_2]_n\cdot CH_2\cdot OH$, is possible in this dehydration, owing to the tertiary nature of the hydroxylated carbon atom: if water is eliminated with the formation of a double bond, the Markownikow rule will ensure that any re-addition of water will give the original alcohol [$\cdot CH_2\cdot C(OH)Me_2 \xrightarrow{-H_2O} \cdot CH{:}CMe_2 \xrightarrow{+H_2O} \cdot CH_2\cdot C(OH)Me_2$]. In consequence only six-membered rings can arise. The six-membered nature of the subsequent thiopyran rings has been confirmed by the identity of their infra-red spectra with those of necessarily six-membered cyclic sulphides derived from hydrogen sulphide addition to di-isoprenes (Sutherland and Sheppard, in the press; Naylor, in the press).

framework. This was accomplished by the following steps, starting from methyl hydrogen glutarate:

$$CO_2Me\cdot[CH_2]_3\cdot CO_2H \xrightarrow{SOCl_2} CO_2Me\cdot[CH_2]_3\cdot COCl \xrightarrow{EtCdBr} CO_2Me\cdot[CH_2]_3\cdot COEt \quad (II.)$$

$$\xrightarrow{MeMgI} CMe_2(OH)\cdot[CH_2]_3\cdot C(OH)EtMe \quad (III.) \xrightarrow{H_2SO_4}$$

(IV.) $Me_2C(O)\cdot CH_2\cdot CH_2\cdot CH_2\cdot CEtMe$ $\xrightarrow{P_2S_5}$  (V.)

Clutterbuck and Raper (*Biochem. J.*, 1925, **19**, 393) report the preparation of methyl δ-ketoheptoate (II) by reaction of ethylzinc iodide with the half-ester half-acid chloride of glutaric acid, but do not record yield. In the present work the zinc alkyl was replaced by ethylcadmium bromide, which reacted with the acid chloride group while leaving the ester group untouched, and a satisfactory yield (58%) of the δ-keto-ester (II) was isolated. By reaction with 3 mols. of methylmagnesium iodide (II) was converted into 2 : 6-*dimethyloctane*-2 : 6-*diol* (III), which condensed in the presence of warm dilute acid to 2 : 2 : 6-*trimethyl*-6-*ethyltetrahydropyran* (IV). The final stage was treatment of (IV) with phosphorus pentasulphide to yield 2 : 2 : 6-*trimethyl*-6-*ethyltetrahydrothiopyran* (V).

The tetrahydrothiopyrans are quite stable towards acids and alkalis, but oxidise slowly in air. They unite with methyl iodide in the cold, but the resulting methiodides often separate as oils, which are difficult to crystallise. The rings of the sulphides (I) and (V) open when the compounds are heated with methyl iodide, the sulphur being removed as trimethylsulphonium iodide. This behaviour is in contrast to the stability of cyclic sulphides, containing primary α-carbon atoms, and is interesting in comparison with the formation of trimethylsulphonium iodide by the action of methyl iodide at 15° on compounds containing the diallylic sulphide grouping, ·CH:CH·CH$_2$·S·CH$_2$·CH:CH· (Selker and Kemp, *Ind. Eng. Chem.*, 1944, **36**, 17). The di-iodide (VI) was not isolated and is probably too unstable to be obtained in the pure state.

$$Me_2C(S)\cdot CH_2\cdot CH_2\cdot CH_2\cdot CMe_2 + 3MeI \longrightarrow SMe_3I + CMe_2I\cdot[CH_2]_3\cdot CIMe_2 \quad (VI.)$$

Experimental.

(Microanalyses were carried out by Dr. W. T. Chambers, Miss H. Rhodes, and Miss E. Farquhar.)

Pentamethylene Sulphide.—Pentamethylene bromide was prepared from piperidine by the method described in *Organic Syntheses*, Coll. Vol. I, pp. 93, 419. A solution of the bromide (40 g.) and anhydrous sodium sulphide (50 g.) in ethanol (250 ml.) was refluxed for 3 hours. After addition of excess of water the product was extracted with ether and twice distilled. Pentamethylene sulphide (6 g., 34%) was obtained as a liquid, b. p. 140°/756 mm., $n_D^{20°}$ 1·5055 (Found: C, 59·0; H, 10·0; S, 31·3. Calc. for $C_5H_{10}S$: C, 58·9; H, 9·8; S, 31·4%).

Synthesis of 2 : 2 : 6 : 6-*Tetramethyltetrahydrothiopyran* (I).—(a) *Action of sodium sulphide on* 2 : 6-*dibromo*-2 : 6-*dimethylheptane.* Magnesium (4·5 g.) under ether was dissolved in a solution of methyl iodide (270 g.) in ether (350 ml.), and to the cooled solution of methylmagnesium iodide was introduced with stirring ethyl glutarate (64 g.) in ether (75 ml.). When the reaction moderated, the solution was refluxed for 1 hour, left overnight, and then poured slowly into aqueous ammonium chloride (200 g. in 700 ml.) containing crushed ice (2000 g.). 2 : 6-Dimethylheptane-2 : 6-diol was extracted with ether both before and after concentration of the aqueous solution, and was obtained from this extract as the monohydrate (30 g.) which was distilled at 85°/1 mm. to give the anhydrous alcohol (21 g.), m. p. 76°. Dry hydrogen bromide was bubbled through an ethereal solution of the alcohol at 0°; after neutralisation of excess acid with sodium hydrogen carbonate, 2 : 6-dibromo-2 : 6-dimethylheptane crystallised out in white needles, m. p. 34° (Found: C, 38·1; H, 6·4. Calc. for $C_9H_{18}Br_2$: C, 37·8; H, 6·3%). The dibromide lost hydrogen bromide very readily, even at room temperature, under reduced pressure. A solution of sodium sulphide (20 g.) and the dibromide (5 g.) in ethanol (50 ml.) was refluxed for 2½ hours, then diluted with water and ether extracted. The extract contained geraniolene (b. p. 40°/13 mm.) and impure 2 : 6-diethoxy-2 : 6-dimethylheptane (b. p. 70°/13 mm.; $n_D^{18°}$ 1·4452), but no sulphur-containing compounds. By heating together the dibromide (5 g.) and dry powdered sodium sulphide (25 g.) for 5 hours at 100—110° was obtained a mixture of geraniolene (b. p. 38°/12 mm.), impure bromo-2 : 6-dimethylheptene (b. p. *ca.* 50°/1 mm.; $n_D^{18°}$ 1·4748), and unchanged dibromide (b. p. 72°/1 mm.; m. p. 24°).

(b) *Action of phosphorus pentasulphide on* 2 : 2 : 6 : 6-*tetramethyltetrahydropyran.* 2 : 6-Dimethylheptane-2 : 6-diol (15 g.), prepared as above, was shaken with 2N-sulphuric acid at 100° for 3 hours; the product contained unchanged diol, geraniolene, and 2 : 2 : 6 : 6-tetramethyltetrahydropyran, b. p. 48°/1 mm. The last (7 g.) was sealed with phosphorus pentasulphide (24 g.) in a nitrogen-filled Carius tube, and heated for 6 hours at 110—120°. The product was extracted with aqueous alkali, dried over potassium carbonate, and distilled. After redistillation 2 : 2 : 6 : 6-*tetramethyltetrahydrothiopyran* (I) (2 g.) was obtained as a colourless liquid, b. p. 66°/12 mm., $n_D^{18°}$ 1·4763 (Found: C, 68·3; H, 11·6; S, 20·1. $C_{10}H_{20}S$ requires C, 68·4; H, 11·4; S, 20·2%). On standing for 1—3 days at 0° with twice its

own volume of methyl iodide, the product yielded white crystals of a *methiodide*, which recrystallised from ethanol–petrol (b. p. 60—80°) on cooling below − 20°; m. p. 130° (decomposition occurred from 130° to 150°) (Found: I, 40·8. $C_{11}H_{23}IS$ requires I, 40·5%). Reaction with excess of methyl iodide for 16 hours at 100° gave crystals, which after being washed with a little methanol and recrystallised from ethanol (absolute) yielded needles of trimethylsulphonium iodide, decomp. *ca.* 200° (Found: I, 61·8; S, 15·5. Calc. for C_3H_9IS: I, 62·2; S, 15·7%).

Synthesis of 2 : 2 : 6-*Trimethyl*-6-*ethyltetrahydrothiopyran* (V).—*Glutaric anhydride.* Glutaric acid (290 g.) and acetic anhydride (400 ml.) were heated under reflux for 2 hours; the acetic acid was then distilled off, and the heating continued with a further 300 ml. of acetic anhydride. After removal of the acetic acid and anhydride, glutaric anhydride (235 g., 96%) was distilled over at 150°/10 mm. [Despite the claims of Krafft and Noerdlinger (*Ber.*, 1889, **22**, 817) that glutaric acid is wholly dehydrated by refluxing alone for 2—3 hours, it was not found possible to complete the conversion into the anhydride by this method.]

Methyl hydrogen glutarate (see Clutterbuck and Raper, *loc. cit.*). Glutaric anhydride (235 g.) and methanol (132 g., 2 mols.) were refluxed for 1 hour, and the product, after removal of methanol, was distilled at 10 mm. The distillate consisted of methyl glutarate, methyl hydrogen glutarate, and some glutaric acid. The first and the last fraction were combined with glutaric acid extracted from the residue, and were reconverted into glutaric anhydride (*via* the acid) and re-esterified with methanol. The overall yield of methyl hydrogen glutarate was 240 g. (80%), b. p. 147—151°/10 mm., $n_D^{20°}$ 1·4372.

Glutaric acid half ester half chloride. A mixture of the acid ester (240 g.) and thionyl chloride (720 g.) was warmed until gas evolution started, and then very gently for one hour and refluxed for a further hour. After removal of excess thionyl chloride, the product (258 g., 97%) distilled at 98°/10 mm.

Methyl δ-Ketoheptoate (II).—An ethereal solution of ethylmagnesium bromide was prepared from magnesium (42 g.) and ethyl bromide (188 g.). Powdered cadmium chloride (288 g.), rendered completely anhydrous by being heated for 1 hour on a sand-bath and allowed to cool in a desiccator over phosphoric oxide, was slowly added with stirring to the Grignard solution cooled in ice. When the solution set nearly solid it was necessary to add more ether and shake vigorously during the addition of the remaining chloride. The ice-bath was then removed, and the mixture stirred for 30 minutes. Absence of excess of Grignard reagent was ensured by testing with Michler's ketone.

To the solution of ethylcadmium bromide (10% excess reckoned on cadmium chloride) at 0° was slowly added with vigorous stirring the half ester half chloride (258 g.) in ether (300 ml.). When the mixture set solid more ether was introduced, and the addition was continued with constant shaking. After refluxing for 1 hour on the steam-bath, the mixture was diluted with ice, and then dilute sulphuric acid was added until the precipitate just dissolved. The ether layer was separated and was shaken successively with dilute aqueous ammonia, dilute sulphuric acid, dilute aqueous sodium hydrogen carbonate, and water. After drying over magnesium sulphate and removal of ether, the product was distilled at 104—110°/10 mm. Refractionation gave 144 g. (58%) of methyl δ-ketoheptoate, b. p. 108°/10 mm., $n_D^{20°}$ 1·4296. On standing for several days with semicarbazide hydrochloride and potassium acetate in aqueous alcohol, the ester yielded a *semicarbazone*, which recrystallised from 95% alcohol to give colourless plates, m. p. 113° (Found: C, 50·2; H, 7·9; N, 19·6. $C_9H_{17}O_3N_3$ requires C, 50·2; H, 7·9; N, 19·6%).

2 : 6-*Dimethyloctane*-2 : 6-*diol* (III).—An ethereal solution of methylmagnesium iodide (3·25 mol.), prepared from magnesium (40·5 g.) and methyl iodide (236 g.), was stirred at 0° during the gradual introduction of methyl δ-ketoheptoate (70 g.) in ether (100 ml.). When addition was complete, the solution was refluxed for 4 hours and then allowed to stand over the week-end. The product was decomposed with a solution of ammonium chloride (105 g.) in water (1500 ml.) at 0°, and the ether layer was separated. The aqueous layer was evaporated down to *ca.* 1200 ml., and constantly extracted with ether for 40 hours. After drying, and removal of ether, the 2 : 6-*dimethyloctane*-2 : 6-*diol* from the combined extracts was distilled at 87—90°/0·1 mm. The diol (60 g., 78%) was a colourless viscous liquid, $n_D^{20°}$ 1·4563, which at 0° slowly crystallised to give an oily white solid, m. p. 25—37°, and slowly sublimed at 20°/10^{-5} mm. to white crystals, m. p. 47—49·5° (Found: C, 68·1; H, 12·2. $C_{10}H_{22}O_2$ requires C, 69·0; H, 12·6%).

2 : 2 : 6-*Trimethyl*-6-*ethyltetrahydropyran* (IV).—2 : 6-Dimethyloctane-2 : 6-diol (28 g.) was vigorously stirred for 30 minutes at 100° with 2N-sulphuric acid (250 ml.). The residual oil was combined with an ether extract of the aqueous layer, and dried over potassium carbonate. After removal of ether the product (12 g., 48%) distilled over at 65—74°/0·1 mm.; dimethyloctadiene was obtained in the lower-boiling fractions (*ca.* 34°/1 mm.). Refractionation of the product gave 2 : 2 : 6-*trimethyl*-6-*ethyltetrahydropyran*, a mobile, colourless, sweet-smelling liquid, b. p. 89°/10 mm., $n_D^{20°}$ 1·4508 (Found: C, 76·7; H, 12·8. $C_{10}H_{20}O$ requires C, 76·9; H, 12·8%).

2 : 2 : 6-*Trimethyl*-6-*ethyltetrahydrothiopyran* (V).—An intimate mixture of 2 : 2 : 6-trimethyltetrahydropyran (12 g.) and phosphorus pentasulphide (35 g.) was heated for 5 hours at 100° in a Carius tube sealed under nitrogen. The solid oily residue was extracted thoroughly with ether, then decomposed by water, and the aqueous solution extracted with ether. The ethereal extract was shaken 3 times with 10% aqueous sodium hydroxide and subsequently dried over magnesium sulphate. After removal of ether, the product (3·5 g., 26%) distilled over at 40°/0·2 mm. After 2 further fractional distillations 2 : 2 : 6-*trimethyl*-6-*ethyltetrahydrothiopyran* was obtained as a mobile, colourless liquid with a characteristic odour, b. p. 87°/13 mm., $n_D^{20°}$ 1·4849 (Found: C, 69·6; H, 11·7; S, 18·6. $C_{10}H_{20}S$ requires C, 69·8; H, 11·6; S, 18·6%). When this was kept with methyl iodide at 0°, the methiodide slowly separated as a red oil, but reaction at 100° (20 hours' reaction in a tube sealed under nitrogen) gave trimethylsulphonium iodide (Found: C, 15·7; I, 61·9. Calc. for C_3H_9IS: C, 15·7; I, 62·2%).

This paper forms part of a programme of fundamental research undertaken by the Board of the British Rubber Producers' Research Association. The author wishes to express his thanks to Dr. E. H. Farmer for his helpful advice and criticism.

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48, Tewin Road, Welwyn Garden City, Herts.

[*Received, November 26th*, 1946.]

NOTES.

Activating Influence of para*-Groups on the Lability of Chlorine in Chlorobenzenes.*

By G. M. Badger, J. W. Cook, and (Miss) Wendy P. Vidal.

In another investigation, the activating influence of the azo-group on a *p*-chloro-substituent towards reaction with an anionoid reagent (compare Borsche and Exss, *Ber.*, 1923, **56**, 2353) appeared to be somewhat greater than expected, and the present work was undertaken to obtain a quantitative measure of this effect. For this purpose, the percentage reaction with piperidine of various *p*-substituted chlorobenzenes has been determined, under standard conditions, by the gravimetric estimation of the halide ion in the reaction mixture, a method essentially the same as that used by Sandin and Liskear (*J. Amer. Chem. Soc.*, 1935, **57**, 1304). A preliminary trial of the method of Brewin and Turner (*J.*, 1928, 332), which involves weighing the piperidine salt which separates out on cooling the reaction mixture, gave much lower results than were obtained by the method of Sandin and Liskear. This was, no doubt, due to the uncertainty as to the composition of the precipitated salt (Powell and Dehn, *J. Amer. Chem. Soc.*, 1917, **39**, 1717), and also to the fact that piperidine hydrochloride is not completely insoluble in benzene.

Materials.—As solvent, sodium-dried, thiophen-free benzene, was used. Piperidine was dried over potassium hydroxide and kept over this reagent after being distilled. The *p*-chloronitrobenzene was a commercial sample, recrystallised from alcohol, m. p. 83°. *p*-Chloroaniline was also a commercial sample, recrystallised from benzene, m. p. 70°. *p*-Chloroazobenzene, prepared by the method of Jacobson and Loeb (*Ber.*, 1903, **36**, 4090) and recrystallised from alcohol, had m. p. 89°. *p*-Chlorobenzonitrile was prepared from *p*-chlorobenzamide by dehydration with phosphoric oxide; recrystallised from aqueous alcohol, it had m. p. 91°. Chlorobenzene was redistilled, b. p. 130°.

Method.—The *p*-substituted chlorobenzene (0·024 mol.) was heated under reflux in an all-glass apparatus, with piperidine (0·1 mol.) in anhydrous benzene (50 c.c.) for 8 hours. The aqueous extract, after being washed with a little benzene, was acidified with dilute nitric acid (5 c.c.) and the halide precipitated as silver chloride with 0·1N-silver nitrate. The precipitate was collected in a Gooch crucible and dried at 100°.

Results.—The following percentage reactions were obtained: *p*-chloronitrobenzene, 12·9, 12·9%; *p*-chlorobenzonitrile, 5·0%; *p*-chloroazobenzene, 1·97, 1·96%; chlorobenzene, 1·29, 1·31%; *p*-chloroaniline, 1·23, 1·24%.

The activating influence of the azo-group is, under these conditions, less than that of the cyano-group, and considerably less than that of the nitro-group. The amino-group exerts little effect.

One of us (G. M. B.) has been working with an Imperial Chemical Industries Research Fellowship.—University of Glasgow. [*Received, October, 24th*, 1946.]

An Improved Preparation of 1 : 8*-Dinitronaphthalene.* By Herbert H. Hodgson and Edward R. Ward.

Whereas 1 : 8-dinitronaphthalene is scarcely attacked by aqueous sulphide even at 90° (Hodgson and Walker, *J.*, 1933, 1346; E.P. 392,914), it is rapidly converted in methanol suspension by a mixture of sodium sulphide and sodium hydrogen carbonate into sulphide dyes (Hodgson and Ward, *J.*, 1945, 794). When, however, the mixture of 1 : 5- and 1 : 8-dinitronaphthalene obtained by nitration of α-nitronaphthalene (Hodgson and Walker, *J.*, 1933, 721) is treated by the above sodium sulphide–sodium hydrogen carbonate mixture in methanol, in amount just sufficient to reduce the whole of the 1 : 5-dinitronaphthalene (about one-third, as determined by the complete removal of the 1 : 8-isomeride with sodium sulphite), the 1 : 8-dinitronaphthalene is entirely unattacked and remains behind after extraction with hydrochloric acid of the 5-nitro-1-naphthylamine mixed with it. Only one crystallisation of the residue from toluene is necessary for obtaining practically pure 1 : 8-dinitronaphthalene in almost quantitative amount.

The finely divided mixture (10 g.) of 1 : 5- and 1 : 8-dinitronaphthalene was suspended in boiling methanol (150 c.c.) and treated with the reducing agent (14 c.c.) [prepared by dissolution of crystalline sodium sulphide (24 g.) and sodium hydrogen carbonate (8 g.) in water (40 c.c.)] added in one batch, and the boiling was continued for 5 minutes; ice chips were then added quickly to the reddish-brown mixture before pouring it into water (total volume *ca.* 1 l.). No sulphide was present at the end of the reaction. The solid was filtered off, washed with water, and then extracted 4 times with boiling 8% hydrochloric acid (400 c.c. per time); the yield of extracted 5-nitro-1-naphthylamine was 8% of the original mixture and *ca.* 24% of the 1 : 5-dinitronaphthalene originally present. The acid-extracted residue, after being washed with water, was dried, and extracted twice with boiling toluene (200 c.c.); on concentration, the filtered toluene extract afforded 1 : 8-dinitronaphthalene (6·3 g., *i.e.*, 63% of the original mixture and *ca.* 95—96% of the amount of 1 : 8-dinitronaphthalene present; cf. the crude yield of *ca.* 40% obtained by Hodgson and Walker, *loc. cit.*), m. p. 169—171·5°. Increasing the amount of reducing agent beyond that used above lowered the yield of 1 : 8-dinitronaphthalene and also the purity of the 5-nitro-1-naphthylamine.

The authors thank Imperial Chemical Industries Ltd., Dyestuffs Division, for gifts of chemicals, and the Department of Scientific and Industrial Research for a Senior Research Award (to E. R. W.).—Technical College, Huddersfield. [*Received, October 25th*, 1946.]

OBITUARY NOTICE.

BEVAN LEAN.

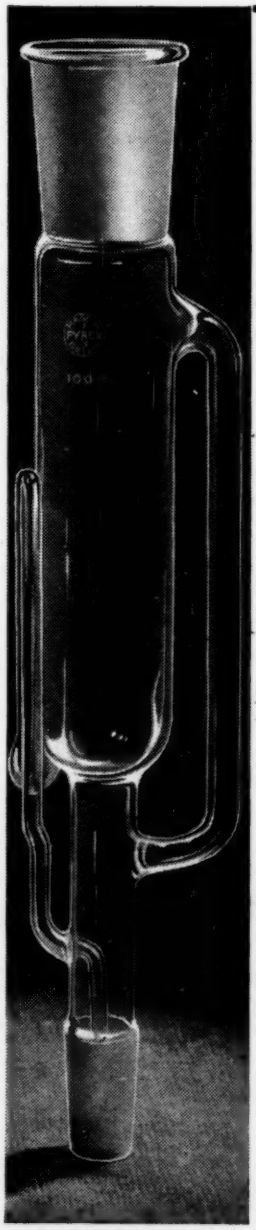
1865—1947

BEVAN LEAN received his early education at Ackworth School, near Pontefract, and at Bootham School, York. He proceeded in 1887 to Owens College, Manchester, to study chemistry, where his exceptional ability was soon recognised. He held the Dalton Scholarship for research in 1891 and the Berkeley Fellowship in 1893, and was appointed to the staff of the Chemistry Department as Assistant Lecturer and Demonstrator in 1894. As a student he was resident at Dalton Hall, and was Tutor in Chemistry there from 1889 to 1894.

During these years at Manchester Lean was actively engaged in research, and was author or part author of six papers in the *Transactions* of the Chemical Society, published in the years 1892—1900. The first of these, with W. A. Bone, was on the " Behaviour of Ethylene on Explosion with less than its own Volume of Oxygen ", but the remainder showed that his chief interest lay in the realm of synthetical organic chemistry and dealt with butanetetracarboxylic acids, their homologues, and derived compounds. He took the external London Degrees of B.Sc. (1889) and D.Sc. (1894).

In 1897 Lean forsook an assured academic future to devote his life to school teaching. After four years as science master at Ackworth, he was appointed Headmaster of the Friends' school at Sidcot, Somerset, a position which he held for twenty-eight years. While there, he published with W. H. Perkin, Junr., in 1909 " An Introduction to Chemistry and Physics ". Lean was himself a lifelong member of the Society of Friends, and was deeply religious. Under his influence the school developed greatly, and the discipline of his scientific training and his whole-hearted devotion to the welfare of the school and the individual scholars combined to make him a headmaster of outstanding ability who won the respect and affection of many generations of Sidcot scholars. He leaves a widow and two sons. The elder, Oscar B. Lean, is in medical practice, and the younger, Owen B. Lean, is an entomologist with Imperial Chemical Industries Ltd.

W. BAKER.



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